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# National Bureau of Standards

Vol. 30, No. 2 February 1943

CONTENTS


| RP | TITLE AND AUTHOR | Page |
|---|---|---|
| 1519. | Analytical separations by means of controlled hydrolytic precipitation. Raleigh Gilchrist..... [Price 5c] | 89 |
| 1520. | Thermal expansion of titanium. Peter Hidnert..... [Price 5c] | 101 |
| 1521. | Modification of the Carius combustion tube to minimize losses by explosion: Pressures attained on heating nitric acid to 300° C. Charles L. Gordon..... [Price 5c] | 107 |
| 1522. | Measuring the degree of curl of paper. F. T. Carson and Vernon Worthington..... [Price 5c] | 113 |
| 1523. | Combination of wool protein with weak acids. Jacinto Steinhardt, Charles H. Fugitt, and Milton Harris..... [Price 5c] | 123 |
| 1524. | pH values of certain phosphate-chloride mixtures, and the second dissociation constant of phosphoric acid from 0° to 60° C. Roger G. Bates and S. F. Acree..... [Price 10c] | 129 |
| 1525. | Miniature Geiger-Müller counter. Leon F. Curtiss.. [Price 5c] | 157 |


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U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1519

*Part of Journal of Research of the National Bureau of Standards, Volume 30, February 1943*

# ANALYTICAL SEPARATIONS BY MEANS OF CONTROLLED HYDROLYTIC PRECIPITATION

By Raleigh Gilchrist

ABSTRACT

To ascertain the completeness of precipitation of hydroxides under conditions of controlled alkalinity in the range pH 1 to 10, experiments were made with over forty of the chemical elements.

Discussion is given of possibilities for analytical separation through controlled hydrolytic precipitation.

CONTENTS

| | Page |
|---|---|
| I. Introduction | 89 |
| II. Hydrolytic behavior of the individual elements | 91 |
| III. Separations | 98 |

## I. INTRODUCTION

The advantages to be gained by controlling the alkalinity at which hydrolytic precipitations are made in analytical chemical operations do not appear to have been fully realized, nor have the possibilities for effecting separations thereby been sufficiently exploited. Experience in developing analytical procedures for the platinum metals and for dental gold alloys has indicated that much use can be made of the precipitation of hydroxides or hydrated oxides (the two terms are used interchangeably in this paper), if the precipitations are made under conditions of controlled alkalinity.

The control of alkalinity is easily accomplished with the aid of indicators, many of which are available today. Establishment of a definite end point may be attained with buffers or by merely neutralizing the solution with such reagents as sodium hydroxide, sodium carbonate, or sodium bicarbonate. The hydrolytic reaction itself serves to some extent as a buffer by liberating acid as the metal hydroxide is produced. Because of this the acidity of the solution tends to increase as the metal hydroxide is precipitated, so that slight adjustment is usually necessary to establish the final predetermined end point.

To illustrate the advantages of hydrolytic precipitation, consider a few familiar separations. The separation of copper from arsenic by means of polysulfide, for instance, is not sharp, and some copper sulfide tends to dissolve. Precipitation of hydrated copper oxide in a hot solution containing not more than 5 g of sodium hydroxide in 100 ml of solution is sometimes used to effect the separation of copper from arsenic. It is not necessary, however, to operate in a solution as strongly alkaline as this. The separation is easily accomplished if the solution is only as alkaline as pH 10. At this alkalinity a few minutes

of boiling suffices to complete the precipitation and coagulation of the hydrated copper oxide and to produce a precipitate which is easily filtered and washed.

In a similar manner copper is readily separated from selenium and tellurium. Lead likewise is conveniently separated from arsenic, selenium, and tellurium if it is oxidized to the quadrivalent state. In this case the lead separates quantitatively as hydrated dioxide at pH 10.

Tin likewise can be separated from copper without resort to the use of polysulfide. Chlorostannic acid hydrolyzes in acid solution and produces hydrated stannic oxide, precipitation of which is complete in the range pH 1 to 6. By operating at pH 1.5, an acidity far above that at which copper compounds hydrolyze, hydrated stannic oxide almost free from copper is produced. The small amount of adsorbed copper is completely eliminated by hydrolytically reprecipitating the tin from sulfuric acid solution at any acidity between 1 and 1.8 *N*.

Hydrolytic precipitations are also advantageous when dealing with the elements of the ammonium sulfide group. For instance, the separation of chromium from iron is usually accomplished by oxidizing tervalent chromium to chromate, and precipitating the iron as hydroxide. The reaction is customarily performed in fairly strong alkaline solution with the aid of sodium peroxide. A better way to effect the separation is to oxidize the chromium in hot, slightly acid solution by means of sodium bromate, and then to precipitate the iron by neutralizing the solution to pH 10. The conversion of tervalent chromium to chromate is rapid if the solution is slightly acid. Corrosion of the glassware, which occurs in strong alkaline solution, is avoided by operating at pH 10.

Not only iron can be thus separated from chromium but also cobalt, nickel, manganese, titanium, etc., as well as copper and lead. In the separation of aluminum from chromium, neutralization to pH 6.5 establishes the alkalinity most favorable to the minimum solubility of aluminum hydroxide.

In platinum metal analysis, hydrolytic precipitation furnishes the only accurate means of separating rhodium and iridium from platinum. It also enables one to recover osmium, ruthenium, and iridium for determination.

Hydrolytic precipitation is likewise valuable in isolating elements from solutions in which a considerable quantity of alkali salts have accumulated.

The idea of precipitation at definite acidity or alkalinity is not new. For example, Blum,[1] from observations made with a hydrogen electrode and with suitable indicators, found that the precipitation of aluminum hydroxide by ammonium hydroxide is complete in the range pH 6.5 to 7.5. These observations resulted in the specification of conditions suitable for the analytical precipitation of aluminum as hydroxide. The main purpose of the present paper is to direct the analyst's attention to the conditions of alkalinity which permit the quantitative hydrolytic precipitation of many of the metallic elements, and to point out how the hydrolytic method can be utilized in effecting chemical separations.

[1] William Blum, J. Am. Chem. Soc. **38**, 1282 (1916).

## II. HYDROLYTIC BEHAVIOR OF INDIVIDUAL ELEMENTS

To ascertain the completeness of precipitation of the various elements under conditions of controlled alkalinity, experiments with individual elements were made. It was found that the hydrated oxides of many of the metals were quantitatively precipitated within a rather narrow range of alkalinity. No attempt was made to follow the hydrolytic curves to locate the precise pH at which minimum solubility existed. Rather, the experiments were of an empirical nature, and the precipitations were made at definite alkalinities, dependent upon the indicators available.

In general, the experiments were performed as follows: Approximately 100 mg of an element was taken, in the form of one of its common salts. Precipitation was made by carefully neutralizing the boiling solution, 150 to 250 ml in volume, to a predetermined end point. The reagents used for neutralization were sodium hydroxide, sodium bicarbonate, or sodium carbonate. After 5 to 10 minutes of boiling, the final end point was reestablished, if necessary, and the precipitate was removed by filtration through quantitative paper. It is to be noted that ammonium hydroxide was not used. This reagent converts the compounds of certain metals, for example, those of cobalt, nickel, manganese, copper, and the platinum metals, into ammines and not into insoluble hydroxides.

In most instances the filtrates were evaporated to dryness or concentrated to a small volume before subjecting them to test. The terms "quantitative precipitation" or "complete precipitation," as used in this paper, mean that the element in question either was not detected by sensitive tests or that its amount in the filtrate did not exceed 0.1 mg.

Since the direct addition of indicator to the solution was not always feasible, the following simple, convenient, and reliable method of determining the end point was used. The stirring rod was lifted so that its lower end was above the level of the solution in the beaker. A drop of a 0.01-percent solution of the indicator was allowed to run into the drop of liquid which clung to the rod. The end point so observed was for all practical purposes identical with that of the indicator placed in the main body of the solution. In this way there was no loss of material, such as is the case in the usual method of using an "outside indicator."

The indicators used in the experiments here described were sulfonphthalein indicators. In the form of their monosodium salts they are water soluble. These indicators and the color changes which occur on passing from acid to alkaline solution were: Thymol blue, which changes from red to orange at about pH 1.5, and from yellow to blue at about pH 10; brom phenol blue, which changes from yellow to blue at pH 4; brom cresol green, which changes from yellow to blue at pH 4.7; chlor phenol red, which changes from yellow to red at pH 6; brom cresol purple, which changes from yellow to blue at pH 6.3; brom thymol blue, which changes from yellow to blue at pH 7; cresol red, which changes from yellow to pink at about pH 8; and xylenol blue, which changes from yellow to blue at an alkalinity slightly greater than pH 8.

Although the color changes of these indicators may not correspond exactly to the true value of the hydrogen-ion concentration of the solution as measured by physical means, nevertheless, as the indicators have been used in these experiments, they do indicate the degree of alkalinity necessary to produce quantitative precipitation. The end points, therefore, are stated in terms of the indicators rather than in values of pH. It should be noted that both end points of thymol blue are utilized, the one at about pH 1.5 for the precipitation of stannic acid and the other for a great many of the other elements. To avoid unnecessary repetition, the end point of thymol blue without further designation means the one at about pH 10.

With most of the base metals it made little difference whether they were in the form of chloride, nitrate, or sulfate. In the case of those which form highly coordinated compounds, the platinum metals for instance, the nature of the attached acidic groups may influence their behavior on hydrolysis. A clear-cut example of this is the marked difference in behavior of the two compounds of ruthenium, $Na_2[RuCl_6]$ and $Na_2[RuCl_5\,NO]$. The former hydrolyzes easily and completely in boiling solution at pH 6.3 to form hydrated ruthenium oxide. The latter produces no precipitate, since, apparently, these conditions are not sufficient to cause the splitting off of the tightly bound nitroso-group.

The hydrolysis of the platinum-metal complexes, as well as those of a number of other metals, is undoubtedly a stepwise process, and the resulting precipitate may contain acid groups. Furthermore, with the platinum metals and certain base metals, it makes no difference whether the reagent used to reduce the acidity of the solution is sodium hydroxide or sodium carbonate. In some instances, lead for example, the presence of carbonate is extremely important. In using the reagents, no attempt was made to exclude atmospheric carbon dioxide from the sodium hydroxide, nor atmospheric oxygen, since the object was to produce an insoluble precipitate and not one of some definite composition. Unless the analyst desires to prepare a compound of definite composition, it makes little difference to him whether the precipitate is a hydrated oxide or a basic salt, as long as it is completely insoluble at the alkalinities in which he is interested and does not contain the elements which he wishes to eliminate.

The observations on the individual elements which are here recorded were gathered largely in connection with problems arising in the analysis of platiniferous materials. Because of this, the precipitations of the individual elements were made in solutions which contained sodium nitrite or sodium bromate, both of which are used in systematic platinum-metal analysis. Except in a few instances, namely, the platinum metals, gold, lead, chromium, nickel, cobalt, and manganese, the recorded observations would be essentially those of the elements in the absence of nitrite or bromate. In those instances where these reagents influence the normal reaction, notation thereof is indicated. For convenience, the observations are grouped according to the arrangement of the elements in the periodic system.

## GROUP I

*Copper.*—Quantitative precipitation of bulky, flocculent, pale blue hydrated oxide occurs at the end point of cresol red or of xylenol blue.

At increased alkalinity the precipitate shrinks in size and turns dark brownish black. It is completely insoluble at the end point of thymol blue.

*Silver.*—If silver is taken as nitrate or sulfate, sodium hydroxide produces partial precipitation at an alkalinity slightly greater than that corresponding to the end point of xylenol blue. In the presence of nitrite there appears to be no precipitation in solutions less alkaline than the end point of thymol blue.

*Gold.*—When sodium hydroxide is added to a solution of chloroauric acid, no precipitation occurs in solutions less alkaline than the end point of thymol blue. The reducing action of nitrite causes the precipitation of metallic gold, which is complete when the acidity of the solution has been reduced to that of the end point of chlor phenol red.

## GROUP II

*Beryllium.*—There is no precipitation of beryllium hydroxide at the end point of brom phenol blue. Precipitation begins at about the end point of brom cresol green, and it is complete in the range from the end point of chlor phenol red to that of thymol blue.

*Magnesium, Calcium, Strontium, and Barium.*—At alkalinities up to that of the end point of thymol blue, precipitation of magnesium, calcium, strontium, and of barium is incomplete, even in the presence of carbonate.

*Zinc.*—Precipitation of hydrated zinc oxide is not quite complete at the end point of cresol red, but it is quantitative at the end point of thymol blue.

*Cadmium.*—Cadmium is possibly completely precipitated at the end point of cresol red or of xylenol blue, when carbonate is used. Precipitation is not quite complete at either the end point of brom cresol purple or of thymol blue, in the presence of sodium hydroxide or of carbonate.

*Mercury.*—Neither sodium hydroxide nor carbonate produces a precipitate in solutions of mercuric salts at alkalinities less than that of the end point of thymol blue. Precipitation does not begin to occur until the alkalinity greatly exceeds this end point.

## GROUP III

*Aluminum.*—The minimum alkalinity at which aluminum hydroxide is completely precipitated appears to be that of the end point of brom cresol purple. At alkalinities greater than pH 7.5 (about halfway between the end points of brom thymol blue and cresol red), aluminum hydroxide becomes increasingly more soluble.

*Gallium.*—Gallium hydroxide begins to precipitate at an acidity slightly higher than that which is required for indium. Precipitation of gallium is complete at the end point of brom phenol blue and at that of chlor phenol red. The precipitate is entirely redissolved at the end point of xylenol blue.

*Indium.*—Indium hydroxide begins to precipitate at an acidity slightly greater than that of the end point of brom phenol blue. It is quantitatively precipitated in the range between the end points of chlor phenol red and thymol blue.

*Thallium.*—No precipitation occurs with univalent thallium at alkalinities up to that of the end point of thymol blue. The presence of bromate causes incomplete precipitation of a dark-brown compound at the end point of cresol red.

*The Rare Earths.*—No experiments were made with the individual rare-earth elements. It is known, however, that quadrivalent cerium, like thorium, is completely precipitated hydrolytically at about pH 3. Precipitation of the tervalent members appears to begin at about pH 6 and, depending on the basicity of the individual oxides, the range extends to about pH 14, the alkalinity necessary to precipitate lanthanum.

## GROUP IV

*Germanium.*—Solutions of germanium dioxide in hydrochloric acid give no evidence of precipitation in the range from tenth-normal acid to the end point of thymol blue. No precipitation appears to occur at even greater alkalinities.

*Tin.*—Quadrivalent tin is quantitatively precipitated in the form of hydrated stannic oxide from chlorostannic acid in the range from tenth-normal acid to the end point of brom cresol purple. When precipitated within this range of acidity, the hydrated stannic oxide is easily filterable. At alkalinities greater than that of the end point of brom thymol blue, the tin precipitate tends to become colloidal.

*Lead.*—There is no alkalinity at which the hydroxide of bivalent lead is completely insoluble. Precipitation of lead in the presence of carbonate is complete at the end point of xylenol blue.

In the presence of bromate, brown, hydrated lead dioxide is quantitatively precipitated in the range from the end point of brom cresol purple to that of thymol blue. The precipitate is most likely insoluble at even higher alkalinities.

*Titanium, Zirconium, Hafnium, and Thorium.*—No extensive experiments were made with this group of elements. Their salts tend to hydrolyze in acid solution. It was found that in the range studied, between the end points of brom cresol purple and thymol blue, titanium and thorium are completely precipitated, and presumably zirconium and hafnium are also.

## GROUP V

*Phosphorus.*—This strongly acidic element participates in reactions in an anionic complex which forms precipitates with many metals, the solubilities of which depend on the degree of acidity or alkalinity of the solution. The alkali phosphates are soluble, but those formed with lead, for instance, are quantitatively precipitated between the end points of brom phenol blue and thymol blue, the range studied.

*Arsenic.*—Like the phosphates, arsenates produce precipitates with many metals. The alkali arsenates are soluble.

*Antimony.*—Antimony, which is more metallic than arsenic, forms a precipitate on reduction of acidity. Precipitation of a hydrated oxide, however, appears to be incomplete in the range of alkalinity studied.

*Bismuth.*—Precipitation of hydrated bismuth oxide is practically complete at the end point of brom cresol purple. Precipitation appeared to be complete at the end point of xylenol blue, when carbonate was present. When the alkalinity was increased to that of the end point of thymol blue, a small amount of bismuth was found in the filtrate.

*Vanadium.*—No precipitation occurs as acid solutions of sodium vanadate are gradually neutralized to and beyond the end point of thymol blue. Like arsenic and phosphorus, however, vanadium in the form of vanadate does produce precipitates with many metals.

*Columbium and Tantalum.*—No experiments were made with columbium and tantalum. Columbic and tantalic oxides precipitate in strongly acid solutions, and are insoluble at alkalinities less than that of the end point of thymol blue.

## GROUP VI

*Selenium and Tellurium.*—Over the range of alkalinity here considered, solutions of sodium selenate and of sodium tellurate gave no indication of the formation of precipitates. In common with the other oxyacid anions, selenates and tellurates do form precipitates with certain metals.

*Chromium.*—Characteristic tervalent chromium hydroxide is quantitatively precipitated at the end point of thymol blue, and possibly so at the end point of xylenol blue.

In slightly acid solution tervalent chromium is easily and completely oxidized by bromate to the chromate state. In this state of valency chromium is completely soluble over the range of alkalinity studied. Formation of insoluble chromates, which occurs when certain cations are present, will be discussed later. Nitrite, in slightly acid solution, reduces chromate to tervalent chromium.

*Molybdenum and Tungsten.*—No precipitation occurs in solutions which contain sodium molybdate or sodium tungstate. Here again, however, certain metals do form precipitates with the tungstate and molybdate radicals.

*Uranium.*—If uranyl nitrate is taken, complete precipitation of a yellow compound appears to be obtained at the end point of xylenol blue. The presence of carbonate causes incomplete precipitation.

## GROUP VII

*Manganese.*—Bivalent manganese is quantitatively precipitated at the end point of thymol blue, and possibly so at the end point of xylenol blue.

In the presence of bromate, brownish hydrated dioxide of manganese is quantitatively precipitated at the end point of xylenol blue.

*Rhenium.*—There was no evidence of precipitation as acid solutions containing perrhenate were gradually neutralized to the end point of thymol blue.

## GROUP VIII

*Iron.*—Precipitation of hydrated ferric oxide is quantitative from the end point of brom phenol blue to and beyond that of thymol

blue. Precipitation is likewise complete in solutions which contain nitrite.

*Cobalt.*—Bivalent cobalt is completely precipitated as a pale pink hydrated oxide at the end point of thymol blue.

The presence of bromate causes the quantitative precipitation, at the end point of xylenol blue, of a brownish,black hydrated oxide in which the valency of cobalt is probably three. This precipitate most likely remains insoluble at alkalinities greater than that of the end point of thymol blue.

Nitrite converts bivalent cobalt salts to nitrito-complexes. Complete decomposition of the nitrito-complex does not appear to be attained at the end point of cresol red, but it is at that of thymol blue. At this latter alkalinity the cobalt is quantitatively precipitated as a dirty-brown hydrated oxide.

*Nickel.*—Bivalent nickel is quantitatively precipitated as a pale-green gelatinous hydroxide at the end point of cresol red. It is likewise insoluble at the end point of thymol blue.

Bromate causes the formation of a black, well-coagulated hydrated oxide, precipitation of which is quantitative at the end point of cresol red. This precipitate, in which the nickel is most likely tervalent, is insoluble at the end point of thymol blue, and most likely so at even higher alkalinities.

Nitrite has no effect, since apparently the nitrito-complex of nickel is less stable than that formed by cobalt, and complete decomposition of it is readily attained.

*Ruthenium.*—In solutions containing ruthenium as a chlorosalt, *but not as a nitrosochloride*, well-coagulated hydrated oxide is completely precipitated at the end point of brom cresol purple, if the ruthenium is quadrivalent. If the ruthenium is tervalent, quantitative precipitation is likewise obtained, but the precipitate is more flocculent and settles less readily.

The effect of nitrite is to form a coordinated complex the sodium salt of which is soluble. Bromate causes the formation of volatile ruthenium tetroxide, especially if the solution is acid.

*Rhodium.*—Solutions containing tervalent rhodium precipitate yellow, flocculent hydrated oxide on neutralization. In slightly acid solution, bromate oxidizes rhodium, which is normally tervalent, to the quadrivalent state. Immediate neutralization precipitates well-coagulated olive-green hydrated dioxide completely at the end point of brom cresol purple, and the precipitate remains insoluble at the end point of xylenol blue and possibly at higher alkalinities.

Nitrite converts the chloroacids of rhodium to a nitrito-complex, $[Rh(NO_2)_6]^{3-}$. This complex is stable at alkalinities up to pH 12 to 14 and possibly greater.

*Palladium.*—Solutions containing bivalent palladium precipitate a brownish hydroxide on neutralization. Bromate oxidizes bivalent palladium to the quadrivalent state in slightly acid solution. Immediate neutralization precipitates well-coagulated, brown hydrated dioxide. Like that of rhodium, this precipitate is entirely insoluble at the end point of brom cresol purple and at that of xylenol blue.

Nitrite converts the chloroacid of palladium to a nitrito-complex, $[Pd(NO_2)_4]^{2-}$. This complex is stable at the end point of cresol red, but it begins to decompose as the alkalinity approaches that of the end point of thymol blue. At somewhat higher alkalinity it is

probably completely decomposed, with the precipitation of brown hydrated oxide.

*Osmium.*—In solutions containing quadrivalent osmium as chloro- or bromosalt, black hydrated osmium dioxide is completely precipitated hydrolytically in the range of acidity between the end point of thymol blue (in this case, pH 1.5) and that of brom cresol purple. The optimum acidity for analytical precipitation is that of the end point of brom phenol blue.

The effect of nitrite is to form a coordinated complex, the sodium salt of which is soluble. Bromate causes the formation of volatile osmium tetroxide, if the solution is acid.

*Iridium.*—As normally encountered, solutions of iridium in the form of its chloroacids contain both tervalent and quadrivalent iridium. For analytical purposes it is necessary to oxidize the iridium to a higher state of valency to insure complete precipitation on neutralization. The evidence appears to be that the precipitate produced when bromate is present contains the iridium in the sexivalent state. When bromate is added to the solution, the deep-green, almost black, precipitate which is formed is completely insoluble in the range between the end point of brom phenol blue and that of xylenol blue.

As in the case of rhodium and palladium, nitrite converts the chloroacids of iridium to a nitrito-complex, $[Ir(NO_2)_6]^{3-}$. This complex appears to have the same degree of stability as the corresponding rhodium one.

*Platinum.*—As normally encountered in solution, platinum is in the form of its chloro-compound, $H_2[PtCl_6]$.

In contradistinction to the chloro-complexes of palladium, rhodium, and iridium, that of platinum, $[PtCl_6]^{2-}$, hydrolyzes so slowly at the end point of brom cresol purple and at the concentration of platinum usually employed in analytical work that no precipitate appears; at least, the first stages of hydrolysis do not result in the formation of insoluble compounds. Given sufficient time, the chloroplatinate radical does behave in a manner similar to those of the other platinum metals. The effect of bromate appears to be to retard the hydrolysis which normally tends to occur.

Nitrite converts the chloroacid of platinum to a nitrito-complex, $[Pt(NO_2)_6]^{2-}$, whose stability is comparable to those of the nitrito-complexes of rhodium and iridium.

## EFFECT OF FILTER-PAPER EXTRACT ON REPRECIPITATION

In those cases where repeated precipitation is made, special attention should be called to the influence which filter-paper extract has on the precipitation of certain elements when bromate is used. The disturbing effect is strikingly illustrated in the cases of cobalt and nickel. In the bivalent state nickel forms a gelatinous light-green hydrated oxide, and cobalt a pale-pink one. In the presence of bromate these metals are oxidized to a higher state of valency and precipitate as black, well-coagulated oxides. If such compounds are caught on filter paper, and the papers and oxides are digested in diluted hydrochloric acid, the resulting filtrates will contain organic matter. When the hydrated oxides of these metals are then reprecip-

itated in the presence of bromate, the black precipitates first formed change to those characteristic of the bivalent state. If, however, the filters and precipitates are decomposed and fumed with sulfuric and nitric acids, subsequent precipitation, with the addition of bromate, produces the oxidized black hydrated form of the oxides, and these remain stable.

## III. SEPARATIONS

It is not the intention here to outline the separation of each pair of elements, but only to indicate the applicability of the general idea of controlling the alkalinity of the solution in chemical separations.

Controlled hydrolytic precipitation has proved itself valuable in the development of analytical procedures for materials which contain the precious metals. The conversion of the four platinum metals, palladium, rhodium, iridium, and platinum, into their nitrito-complexes enables one to separate these four metals from a considerable number of other elements, merely by adjusting the alkalinity of the solution to that at which the particular element precipitates quantitatively. In general, the hydrated oxides of many of the base metals can be collectively precipitated, since the alkalinities at which they are completely insoluble practically coincide. This set of conditions, upon which a method was based for analyzing materials of the type of dental gold alloys [2], has been successfully used in this laboratory to effect the separation of base metals in the analysis of native platinums.

Other papers [3 4 5] from this Bureau describe fully the precipitation of palladium, rhodium, and iridium as hydrated oxides, either singly or collectively, in their separation from platinum. These papers, as well as others, [6 7 8 9] also describe the hydrolytic precipitation of ruthenium, osmium, rhodium, and iridium for purposes of recovery from solution and of analytical determination.

When certain combinations of elements are in solution, reduction of the concentration of hydrogen ion causes precipitation of salts rather than of hydroxides. This situation occurs when anions of oxyacids are present. The precipitation of these salts is influenced by the degree of acidity or alkalinity of the solution, and in many instances there exist certain ranges of hydrogen-ion concentration over which particular compounds are completely insoluble. For example, lead phosphate was found to be quantitatively precipitated in the range studied, namely, pH 4 to 10. Similarly, lead chromate was found to be entirely insoluble in the range investigated, namely, pH 6.3 to 8. Lead carbonate was found to be insoluble at pH 8 when carbonate was present. Published data on solubilities give that of lead carbonate in water at room temperature as about 1 mg in 1 liter, and that of lead phosphate, as well as that of lead chromate, as about 0.1 mg. In the presence of common ions, these solubilities are undoubtedly still lower. Precipitation of such compounds finds an application in chemical separation, such, for example, as in separating lead from the platinum metals in nitrite solution.

[2] Raleigh Gilchrist, J. Research NBS **20**, 745 (1938) RP1103.
[3] R. Gilchrist, BS J. Research **12**, 291 (1934) RP655.
[4] R. Gilchrist and E. Wichers, IX Congreso Int. quim. pura aplicada **6**, 32 (1934).
[5] R. Gilchrist and E. Wichers, J. Am. Chem. Soc. **57**, 2565 (1935).
[6] R. Gilchrist, BS J. Research **3**, 993 (1929) RP125.
[7] R. Gilchrist, BS J. Research **6**, 421 (1931) RP286.
[8] R. Gilchrist, BS J. Research **9**, 547 (1932) RP489.
[9] R. Gilchrist, BS J. Research **12**, 283 (1934) RP654.

In many instances controlled hydrolytic precipitation effects the separation of those elements which form hydrated oxides from those which form oxyacids. For example, chromium, when oxidized to chromate by sodium bromate, is easily separated from copper, nickel, cobalt, manganese, titanium, aluminum, indium, or zinc, if the individual solution is neutralized to the particular end point of the metal in question. Collective separation is likewise possible, because many of the hydrated oxides are insoluble within the same range of alkalinity.

The separation of lead from elements which form oxyacids is interesting. As previously mentioned, lead is quantitatively precipitated by the chromate ion in the range pH 6.3 to 8. Under the influence of sodium bromate, lead chromate is decomposed when the alkalinity of the solution exceeds pH 7, and hydrated lead dioxide is precipitated. In a like manner, lead sulfate, which is appreciably soluble, is very readily decomposed, with the complete precipitation of hydrated lead dioxide. Similar separations of lead from selenate, tellurate, and arsenate take place. Preliminary experiments indicated that oxidation of lead and the production of lead dioxide resulted when lead phosphate, lead vanadate, and lead molybdate were treated with sodium bromate.

The ease with which the elements that form oxyacids are separated from other metals does not appear to be equal. Arsenic, selenium, and tellurium, in their highest states of valency, are readily separated from copper, for example, at an alkalinity of pH 8 to 10, without the addition of bromate. Vanadium, however, does not seem to be as easily separated; at least, at alkalinities less than pH 10. In all probability operation at a higher alkalinity would be more effective, but sufficient investigation was not made with vanadium to ascertain the necessary conditions.

In the presence of bromate, arsenic is separated from palladium, rhodium, and iridium. A separation of chromium from these three metals can also be effected, if bromate is added to the solution, but a better way is to remove the chromium as tervalent hydroxide in a solution in which the platinum metals have been converted to nitrito-complexes.

An interesting possibility for separation by hydrolytic precipitation appears to be that of copper and zinc from mercury. No precipitation occurs in solutions of mercuric salts which are not too concentrated until the alkalinity of the solution greatly exceeds pH 10. Experiments showed that hydrated zinc oxide and hydrated copper oxide, precipitated at the end point of thymol blue, were not contaminated with mercury. Other separations, which depend solely on differences in alkalinity, likewise can be made, such as that of stannic tin from copper, etc.; and it is most likely possible to effect the separation of germanium from gallium and indium, and of gallium from indium.

WASHINGTON, December 15, 1942.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1520

*Part of Journal of Research of the National Bureau of Standards, Volume 30, February 1943*

# THERMAL EXPANSION OF TITANIUM

By Peter Hidnert

ABSTRACT

This paper gives data on the linear thermal expansion of titanium (97.2 percent) at various temperatures between −190° and +700° C. The coefficient of expansion of titanium increases from about $5\times10^{-6}$/° C at −150° C to about $12\times10^{-6}$/° C at 650° C. The data on thermal expansion do not indicate the existence of polymorphic transformations of titanium between −190° and +700° C.

CONTENTS

| | Page |
|---|---|
| I. Introduction | 101 |
| II. Material investigated | 101 |
| III. Apparatus | 102 |
| IV. Results | 102 |

## I. INTRODUCTION

Very little information is available on the thermal expansion of titanium. The Metals Handbook of the American Society for Metals (1939 edition) gives $7.14\times10^{-6}$/° C for the coefficient of linear thermal expansion of titanium at room temperature. The author has been informed that this value was obtained [1] on a fragment of titanium of "about 98 to 99 percent purity" with the Fizeau-Pulfrich interferometer method between 24° and 153° C. The linear thermal-expansion curve of titanium was found to be practically a straight line for this range of temperature.

In order to obtain data on the linear thermal expansion of titanium over a wider temperature range, an investigation was undertaken at the National Bureau of Standards, and the results at various temperatures between −190° and +700° C are given in this paper.

## II. MATERIAL INVESTIGATED

A plate of cast titanium about 6 inches in diameter and ⅜ inch in thickness was obtained from the Titanium Alloy Manufacturing Co. A number of samples were prepared from this casting for chemical analysis and for determinations of the density and linear thermal expansion. An Alundum abrasive disk, 60 grit-K4L, 8 inches in diameter and ⅛ inch in thickness, was found to be satisfactory for cutting the samples from the plate of titanium. The surfaces of the samples were finished by wet grinding with an Alundum wheel.

[1] By the Titanium Alloy Manufacturing Co., Niagara Falls, N. Y.

The chemical composition [2] of a sample of the cast titanium was found to be as follows: carbon 0.22, manganese 0.01, silicon 1.05, vanadium 0.17, iron 1.11, columbium less than 0.2, copper less than 0.01, titanium (by difference) 97.2 percent. Attempts to obtain a rod or plate of titanium having a purity of 99 percent or higher were unsuccessful.

The densities [3] of two samples were found to be 4.542 g/cm [3] and 4.546 g/cm [3] at 25° C.

Two samples (1641A and 1641B) were used for the determinations of linear thermal expansion. The length of each sample was 15 cm. The cross sections of samples 1641A and 1641B were 20 by 10 mm and 14 by 9 mm, respectively.

## III. APPARATUS

The fused-quartz-tube expansion apparatus described by Hidnert and Sweeney [4] was used for determinations of the linear thermal expansion of sample 1641B over the range −190° to +20° C. Liquid air, solid carbon dioxide in a mixture of equal parts of carbon tetrachloride and chloroform, and ice and water were used for the low-temperature baths at about −190°, −78°, and 0° C, respectively.

Determinations of the linear thermal expansion of sample 1641A were made at various temperatures between 20° and 700° C with the precision micrometric thermal-expansion apparatus described by Souder and Hidnert.[5] Figure 5 of their publication indicates the method used in mounting the sample in the furnace. A platinum-osmium (about 6½ percent of osmium) observation wire 0.002 inch in diameter was placed in a sharp V groove cut near each end of the sample.

## IV. RESULTS

Figures 1 and 2 show the observations on the linear thermal expansion of sample 1641B at low temperatures (−190° to +20° C) and of sample 1641A at elevated temperatures (20° to 700° C). The contraction and expansion curves of sample 1641B at low temperatures were found to coincide. However, the expansion and contraction curves of sample 1641A at elevated temperatures did not coincide. In the first test of the latter sample to 500° C, the observations on cooling were slightly below the expansion curve. In the next test to 700° C, the contraction curve was appreciably above the expansion curve. The heat treatment of the sample incident to the heating and cooling cycle of this test stabilized the sample to such an extent that on a repetition of the test over the same temperature range (20° to 700° C) the observations on cooling were close to the expansion curve.

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[2] Determined by J. L. Hague, of the National Bureau of Standards.
[3] Determined by Mary G. Blair, of the National Bureau of Standards.
[4] P. Hidnert and W. T. Sweeney, *Thermal expansion of magnesium and some of its alloys*, BS J. Research **1**, 771 (1928) RP29.
[5] W. Souder and P. Hidnert, *Measurements on the thermal expansion of fused silica*, BS Sci. Pap. **21**, 1 (1926–27) S524.

The coefficients of expansion of titanium which were derived from the curves in figures 1 and 2 are given in table 1.

TABLE 1.—*Coefficients of linear expansion of titanium*

| Sample | Test | Average coefficients of expansion and contraction per degree centigrade | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | −190° to −80° C | −80° to +20° C | −190° to +20° C | +20° to 60° C | 20° to 100° C | 20° to 200° C | 20° to 300° C | 20° to 400° C | 20° to 500° C | 20° to 600° C | 20° to 700° C |
| | | ×10⁻⁶ | ×10⁻⁶ | ×10⁻⁶ | ×10⁻⁶ | ×10⁻⁶ | ×10⁻⁶ | ×10⁻⁶ | ×10⁻⁶ | ×10⁻⁶ | ×10⁻⁶ | ×10⁻⁶ |
| 1641B | 1, heating | 5.5 | 8.3 | 6.8 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| | 1, cooling | 5.5 | 8.3 | 6.8 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| 1641A | 1, heating | ------ | ------ | ------ | 9.3 | 8.9 | 9.5 | 9.4 | 9.8 | 10.0 | ------ | ------ |
| | 1, cooling | ------ | ------ | ------ | 9.0 | 9.2 | 9.7 | 9.8 | ------ | 10.1 | ------ | ------ |
| | 2, heating | ------ | ------ | ------ | ------ | 8.8 | 9.1 | 9.5 | 9.7 | 10.0 | 10.4 | 10.7 |
| | 2, cooling | ------ | ------ | ------ | ------ | 9.2 | 9.5 | 9.7 | ------ | ------ | ------ | 10.4 |
| | 3, heating | ------ | ------ | ------ | ------ | 9.0 | 9.4 | 9.7 | 9.7 | ------ | 10.1 | 10.5 |
| | 3, cooling | ------ | ------ | ------ | ------ | 9.4 | 9.8 | 9.9 | ------ | ------ | ------ | 10.5 |

Figure 3 indicates the relation between the coefficient of expansion or rate of expansion, of titanium and temperature between −150° and +650° C. The curve is concave toward the temperature axis between −150° and about +50° C, and is linear at higher temperatures. The coefficient of expansion of titanium, $8.5\times10^{-6}$/° C at room temperature, is appreciably higher than the value $7.14\times10^{-6}$ published in the Metals Handbook referred to previously.

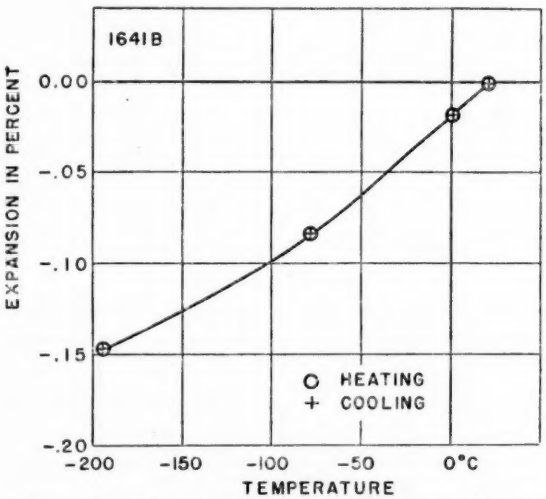


FIGURE 1.—*Linear thermal contraction of titanium on cooling below room temperature, and expansion on subsequent heating from −190° C to room temperature.*

The data on the linear thermal expansion of titanium show no evidence of polymorphic transformations between −190° and +700° C. Koenigsberger and Schilling[6] investigated the electric resistance of titanium between −190° and +800° C and reported polymorphic

[6] J. Koenigsberger and K. Schilling, *Über Elektrizitätsleitung in festen Elementen und Verbinungen. I. Minima des Widerstandes, Prüfung auf Elektronenleitung, Anwendung der Dissoziationsformeln*, Ann. Physik **32**, 179 (1910).

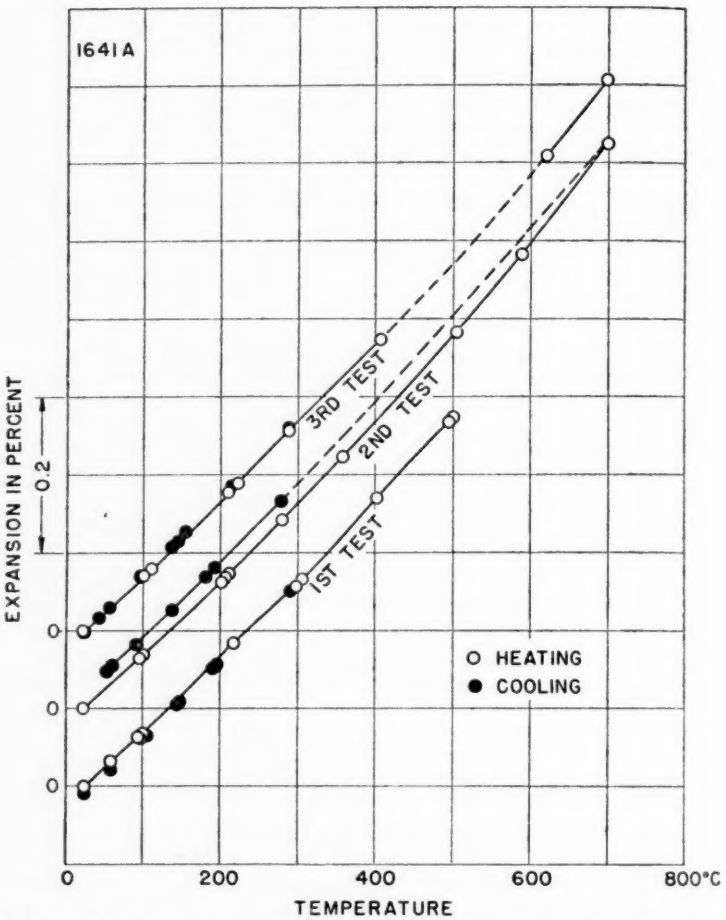


FIGURE 2.—*Linear thermal expansion of titanium at elevated temperatures.*

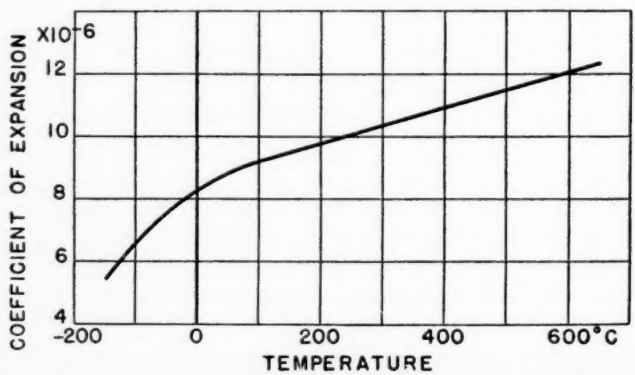


FIGURE 3.—*Relation between coefficient of expansion of titanium and temperature.*

transformations at about 310° and 590° C. Schulze [7] also determined the electric resistance of titanium, but he found no evidence of transformations between 0° and 1,200° C.

In order to secure more evidence on the presence or absence of polymorphic transformations in titanium, a small specimen cut from the plate of titanium was heated to 720° C and then cooled to room temperature.[8] The time-temperature curves show no evidence of transformations, either on heating or cooling of the specimen.

WASHINGTON, September 5, 1942.

[7] A. Schulze, Umwandlungserscheinungen an sogenannten Halbleitern, Z. Metalkunde **23,** 261 (1931) or *Über die Umwandlungen von Metallen,* Z. Vereines deut. Ing. **76,** 108 (1932).

[8] By S. J. Rosenberg, of the National Bureau of Standards.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1521

*Part of Journal of Research of the National Bureau of Standards, Volume 30, February 1943*

# MODIFICATION OF THE CARIUS COMBUSTION TUBE TO MINIMIZE LOSSES BY EXPLOSION: PRESSURES ATTAINED ON HEATING NITRIC ACID TO 300° C

By Charles L. Gordon

ABSTRACT

This paper describes a modified form of tube which minimizes the likelihood of loss by explosion in the Carius method of determining halogens and sulfur in organic substances. The familiar Carius tube of Pyrex glass cannot be sealed properly in the laboratory. Residual strains in the glass seals cause the tubes to burst at pressures much lower than those to be expected from the normal strength of the glass. By sealing smaller neck-tubes on the usual heavy-walled tubes, all the seals except the small final seal can be oven-annealed at the factory.

While the bursting pressure of the unmodified tubes was found to be between 1,000 and 1,400 pounds per square inch, the modified tubes burst at over 2,500 pounds per square inch. The pressures developed during a Carius determination were estimated from determinations of the pressures developed by various amounts of fuming nitric acid in a specially designed gage. Such pressures were found to be below 1,520 pounds per square inch at temperatures up to 300° C when the amount of acid was limited to that customarily used.

A difficulty which limits the usefulness of the Carius method for the determination of halogens and sulfur in organic substances is the frequent breakage of the tubes during the decomposition with fuming nitric acid. This is so well known that the procedure has been referred to as the "precarious method." In connection with the use of sealed tubes for the decomposition of some minerals and refractory metallic substances with hydrochloric acid [7],[1] observations were made which appeared to explain the frequent failures of Carius tubes and which suggested a simple modification that will obviate most such failures.

Carius tubes as supplied in Pyrex laboratory glass are long, heavy-walled tubes, ranging up to 19 mm in inside diameter, and with a constriction near the open end to facilitate sealing. The bursting pressure of several of these tubes of 15-mm inside diameter (wall thickness approximately 2.5 mm), when sealed with reasonable care but without special attention to annealing, ranged from 1,000 to 1,400 pounds per square inch. An effort was made to "smoke" some of these seals, but difficulties in handling the filled tubes precluded any good smoking operation. The bursting pressure of tubes sealed without smoking have not differed noticeably from those "smoked."

[1] Numbers in brackets indicate the literature references at the end of this paper.

Measurements of bursting pressure were made by heating the tubes, half-filled with water, in a loosely capped piece of pipe supported in a combustion furnace [2] until steam suddenly escaping through the loosely fitted cap indicated bursting of the tube. Temperatures were measured by means of a thermocouple hard-soldered to the pipe. The corresponding pressures were taken from a table of saturated water vapor pressures [5] if below the critical temperature, or from a table of the pressure of dilated water vapor [2] if above the critical temperature. Although the bursting pressures are thus measured at different temperatures, they were considered to be comparable, since the strength of Pyrex glass is nearly constant below 400° C.

The bursting pressure of well-annealed glass tubes of the dimensions given, and made with well-rounded ends, is over 3,000 pounds per square inch, calculated on the basis of a tensile strength of about 10,000 pounds per square inch [4]. It is well known that the actual strength of glass is affected by the presence of scratches or other imperfections and by strains. With the tubes in question, careful attention was given to keep the surface free from scratches, but it became evident that the ends of the tubes, sealed with the contents of the tube in place, could not be adequately annealed. A modified form of tube was then made by attaching to the open end a tube of 4-mm inside diameter and 2-mm wall thickness (4 by 8 mm). The tube thus made was oven-annealed before use. The tube was charged through this neck of smaller bore and sealed without any attempt at annealing.

Tubes made in this way did not burst at pressures of water vapor less than 3,100 pounds per square inch. Sections of the 4- by 8-mm tubing alone, with both ends sealed without special precautions, burst at pressures greater than 5,000 pounds per square inch. This is about one-half the theoretical bursting pressure calculated on the basis of a tensile strength of 10,000 pounds per square inch. Several pieces of standard-wall tubing 7- by 9.5-mm burst at about 2,100 pounds per square inch, which is 50 to 100 percent above the pressure at which the unmodified Carius tubes burst. If Carius tubes are made with attached necks of 6-mm inside diameter and 9- to 10-mm outside diameter, failures by bursting should be very infrequent. Such tubes are also easier to seal and easier to open for removal of the contents than those now available. An inside diameter of the neck of 6-mm is sufficient to allow easy introduction of the sample in a glass capsule.

In order to estimate the pressure that may occur in Carius tubes, measurements were made of the pressures developed by fuming nitric acid in sealed tubes at temperatures up to 300°C. These measurements were made by enclosing the acid in a glass U-tube with the bend flattened like a Bourdon tube. A change in pressure within the tube caused movement of the arms, which was balanced by a compensating gas pressure within a steel bomb and observed by the opening or closing of an electrical circuit through a pair of platinum-iridium contacts attached to the ends of the arms. The compensating pressures were read on a Bourdon gage to within 5 pounds per square inch.

Since nitric acid is not a single-component system, the pressures generated by different amounts of the acid in a given total volume are different. Two sets of measurements of the pressures generated by

[2] Carius decompositions can be conducted in a similar manner, if the customarily used bomb furnace is not available. The pipe can be made the furnace itself by covering it with a layer of asbestos paper over which is wound a spiral of resistance wire and several more layers of asbestos paper.

fuming nitric acid (sp gr at 25° C of 1.48) are shown in figure 1. The two curves are for different "mean densities", which are the total grams of nitric acid solution per 100 ml of total volume. Curve A shows the pressures attained by 63.2 g of acid per 100 ml (or 42.7 ml/100 ml at 25° C). This quantity is nearly that mistakenly recommended for use in the Carius procedure by some textbooks [1]. Curve B shows the pressures developed when the amount of acid is equal to the maximum of 8 g/100 ml suggested by Fresenius [3]. These pressures may be taken as indicative of the maximum pressure developed in a Carius determination on the assumption that the addition of the silver nitrate and the organic material affect the total pressure but slightly. From figure 1 it can be seen that in the temperature range 200° to 300° C the pressures developed are in the bursting range of the unmodified tubes previously mentioned.

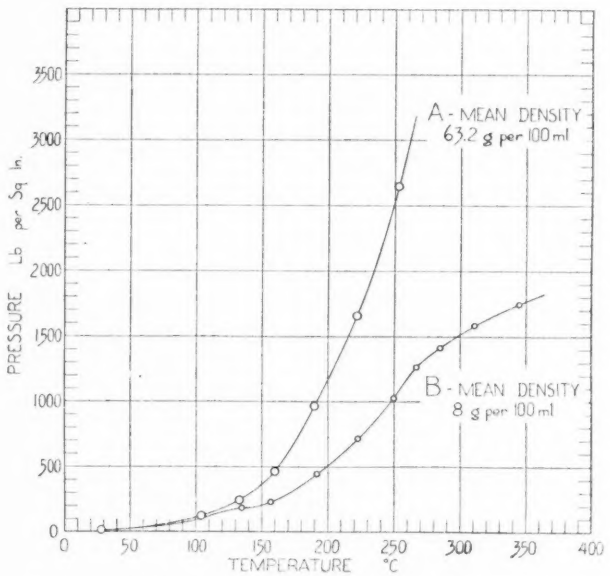


FIGURE 1.—*Pressures developed by fuming nitric acid (sp gr 1.48 at 25° C) at constant volume on heating.*

The mean density is the total amount of acid as vapor and as liquid in the tube per unit volume (100 ml).

The results from which the curves in figure 1 were constructed, together with those for one additional quantity of nitric acid, are given in table 1. Although they are not of high precision, they may be useful, especially in connection with the design of apparatus, in view of the absence of other recorded data on the pressures developed by nitric acid at elevated temperatues.

To show whether there is liquid present in the tube as used in a Carius determination when the amount of fuming nitric acid is 8 g/100 ml or less, small tubes containing various quantities of the fuming nitric acid were prepared. These were heated in a vertical glass cylinder on which was wound a resistance wire as the heating element. A thermocouple suspended in the cylinder beside the sealed

TABLE 1.—*Pressures developed at constant volume by various amounts of fuming nitric acid (sp gr 1.48 at 25° C)*

| Amount of acid | | | | | |
|---|---|---|---|---|---|
| 63.2 g/100 ml | | 18.9 g/100 ml | | 8.0 g/100 ml | |
| Temperature | Pressure (abs.) | Temperature | Pressure (abs.) | Temperature | Pressure (abs.) |
| °C | lb/in.² | °C | lb/in.² | °C | lb/in.² |
| 133 | 245 | 133 | 180 | 157 | 230 |
| 160 | 465 | 165 | 380 | 192 | 445 |
| 190 | 965 | 192 | 630 | 223 | 715 |
| 222 | 1,655 | 219 | 995 | 250 | 1,025 |
| 253 | 2,645 | 256 | 1,565 | 267 | 1,265 |
| | | 285 | 2,245 | 285 | 1,415 |
| | | 313 | 2,945 | 311 | 1,585 |
| | | 326 | 3,135 | 345 | 1,745 |

tube was used to measure the temperature at which (without agitation) the last trace of the liquid phase disappeared. Figure 2 shows these "dew-point" temperatures plotted against the "mean density." The tube with the highest mean density was the only one in which the meniscus disappeared before it reached the bottom of the tube.

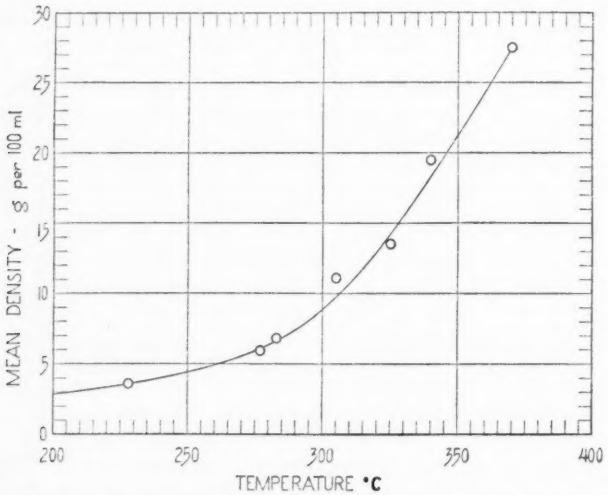


FIGURE 2.—*Dew-point temperatures of fuming nitric acid (sp gr 1.48 at 25°C).*

The modified design for the Carius tube is shown in figure 3. The stem is carefully sealed to a heavy-walled Pyrex tube with well-rounded shoulders. The other end is a well-rounded seal. The

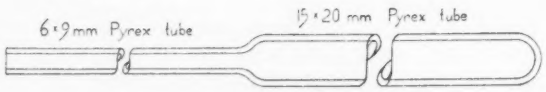


FIGURE 3.—*Modified Carius tube.*

The volume of the main tube is approximately 0.57 ml/cm, the tube is made of such length as will permit the desired amount of nitric acid to have a mean density of 8 g/100 ml or less. The length of the neck, if 15 cm, is sufficient to permit repeated use of the tube.

whole tube is flamed to eliminate any minute surface scratches. It is then carefully annealed by heating to 560° to 580° C and maintaining within this temperature interval for at least 1 hour, followed by slow cooling [6]. The tubes thus made should be kept individually wrapped, to prevent scratching of the finished surface while they are stored before use.

For the final sealing of the tube, a simple and satisfactory technic is as follows: Clamp the tube in a vertical position. Warm the neck slightly below the open end to cause an expulsion of air. Heat the open end until it flows together. A very hot flame (oxygen-gas) is necessary for this so that the end will fuse completely without leaving a pinhole. The fused end may suck back slightly but can be blown out round by rewarming the neck below the seal and applying the hot flame across the top of the seal to heat the thickened portion, but not the sides. Skill in making such seals can be acquired with a little practice on pieces of tubing identical with that used for the necks, which have been previously closed at one end.

When decomposition of the organic substance is completed, excess pressure in the tube is released as usual by heating the tip of the seal and allowing it to blow out. A short section of the neck can then be cut off, leaving the main part of the tube intact. The tubes can then be rinsed through the neck by any convenient means. Any silver chloride adhering to the interior of the tube can be removed with ammonium hydroxide. If only a short piece of the neck is cut off to open the tube, the tube can be used for several determinations, inasmuch as nitric acid under pressure and elevated temperature (as contrasted with hydrochloric and hydriodic acids), does not attack the glass to such an extent as to make resealing unfeasable. A tube saved in this manner and used three times was subsequently found to burst at over 4,000 pounds per square inch.

Carius micro determinations can be made in 4- by 8-mm heavy-walled Pyrex tubes sealed without annealing. Such tubes withstand pressures above 5,000 pounds per square inch. The volume can be adjusted as required by using a tube of the necessary length. The capacity of this tubing is approximately 0.125 ml per cm of length. A small capsule of 2- by 3-mm tubing may be used for the sample. In these tubes a larger amount of nitric acid per unit volume is permissible because of the greater strength of the tube.

[1] W. W. Beshgetoor, Ind. Eng. Chem., Anal. Ed. **1,** 92 (1929).
[2] N. E. Dorsey, The Properties of Ordinary Water-substance, table 36, page 87 (Reinhold Publishing Corporation, New York, N. Y., 1940).
[3] C. R. Fresenius, Quantitative Chemical Analysis, vol. II, p. 118, translation of 6th German edition by A. I. Cohn (John Wiley & Sons, New York, N. Y., 1904).
[4] G. W. Morey, The Properties of Glass, p. 330, (Reinhold Publishing Corporation, New York, N. Y., 1938).
[5] N. S. Osborne and C. H. Meyers, J. Research NBS **13,** 1 (1934) RP691.
[6] Pyrex Brand Laboratory Glassware, catalog LP 21, p. 7, Corning Glass Works, Corning, N. Y. (1941).
[7] E. Wichers, W. G. Schlecht, and C. L. Gordon (unpublished work).

WASHINGTON, November 27, 1942.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1522

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# MEASURING THE DEGREE OF CURL OF PAPER

By Frederick T. Carson and Vernon Worthington

ABSTRACT

In a method frequently used to determine the tendency of paper to curl, a measurement is made of the amount of curl of a small piece of the paper floating on water. The measurement is customarily made in terms of an arbitrarily chosen angle. The maximum curvature, however, is a more logical measure of curliness. An effort has been made to determine the maximum curvature of freely curling paper from measurements made of the curling of paper in contact with water, and the new apparatus devised for the purpose is described. Measurements were made of the relative curliness of a number of lithographic papers. The correlation of curl with other related properties is discussed. The results of the measurement of curl agree reasonably well with what is known about the behavior in use of the papers studied.

CONTENTS

| | Page |
|---|---|
| I. Introduction | 113 |
| II. Sources of uncertainty in measuring curling tendency with the curl sizing tester | 115 |
| III. Maximum curvature as a measure of curliness | 116 |
| 1. New apparatus to measure curvature | 116 |
| 2. Estimate of curvature with curl sizing tester | 117 |
| 3. Curl data on lithographic papers | 118 |
| IV. Discussion of curl measurement | 120 |

## I. INTRODUCTION

Trouble arising from the curling of sheets of paper during printing and some other converting processes can often be avoided if one knows beforehand what to expect of the behavior of the paper. A simple test now frequently used for predicting relative curling tendency is made with an instrument developed at the National Bureau of Standards, but which originally was intended for quite a different purpose. This instrument, known as the curl sizing tester, was designed to use the rate of curl of paper, when wet on one side, as a measure of the rate of penetration of water into the paper. In the extended use of the instrument the maximum angular displacement of the specimen is used as an indication of curling tendency. This new use of the instrument has been subject to some uncertainty, for reasons that will be discussed later. An appraisal of its value has therefore been attempted, and some suggestions have been made for improving the test for curling tendency.

The curl sizing tester[1] was devised several years ago to measure the "degree of sizing" of paper (resistance to permeation by water and aqueous solutions). The device contains a wax-coated aluminum

[1] Paper Trade J. **79**, TS142 (1924).

float in which a rectangular aperture allows water to present a convex meniscus standing slightly above the bottom of the float. The principle of operation can be understood from figure 1, which represents a vertical section through the aperture. When a piece of paper is laid over this aperture it becomes wet on one side and curls up. The wet part over the aperture is curved, whereas the part extending beyond the aperture remains dry to serve as a pointer against the stippled background.[2] At the opposite side of the aperture a shorter, dry end of the specimen is held by a stop on the holder, *H*, and makes a fixed angle, *F*, with the plane of the float. In using the instrument as first intended one notes the time which elapses from the contact of the specimen with the water until the pointer attains its maximum sweep and reverses the direction of its movement. This time in-

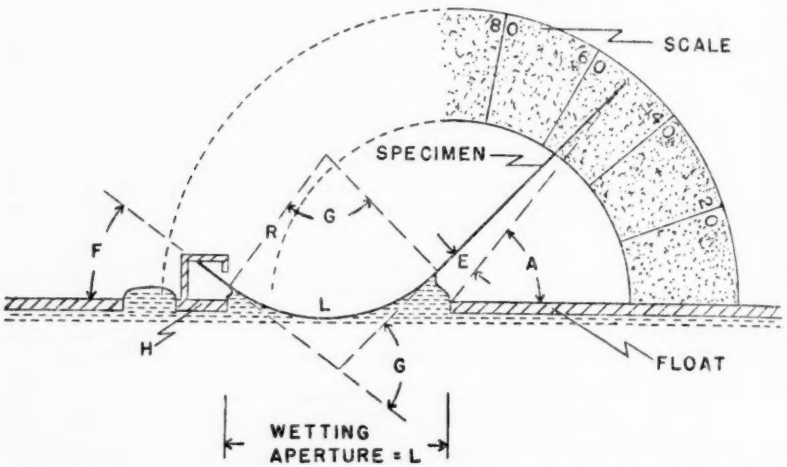


FIGURE 1.—*Sketch, vertical section, illustrating principle of curl sizing tester, and indicating how the apparatus has been adapted to measuring degree of curl.*

terval, interpreted as that required for the water to go halfway through the sheet, is taken as a measure of the relative resistance of papers to the passage of water through them. The wetting aperture is adjustable by means of the sliding holder, *H*, with which the length of the arc, *L*, in figure 1 can be increased or decreased, as required by the nature of the paper, so that the direction of movement of the pointer will be reversed at a convenient location for observation near the middle of the background. A very curly paper requires a narrow opening to prevent it from curling back upon itself, whereas a paper with little curl requires a wide opening to produce a substantial travel of the pointer.

At first there was no thought of any other use of the curl sizing tester, but in time technicians began to note the *amount* of travel of the pointer as a rough measure of the curliness of the paper. They requested the manufacturer of the instrument to add a scale in degrees to facilitate such a reading. A new use of the instrument

[2] To avoid confusion of the lines in figure 1, the left half of the background is not drawn in. There was no scale on the background of the original instrument.

thus arose, wherein the value of angle $A$, figure 1, at the instant the pointer reverses its direction of movement, is used as a measure of the relative curliness of papers.

## II. SOURCES OF UNCERTAINTY IN MEASURING CURLING TENDENCY WITH THE CURL SIZING TESTER

There are some reasons for doubting the value of the scale reading alone (angle $A$, fig. 1) as a measure of curling tendency. This angle is not the one which the paper pointer (tangent to the arc) makes with the plane of the float (the plane of origin of the curling paper), because the stippled background of the curl sizing tester is symmetrical with respect to the fixed edge of the aperture, and the added scale radiates from this fixed edge. Therefore, the paper pointer does not lie on a radial line, and angle $E$ must be subtracted from $A$ to give the angular displacement of the pointer. Angle $E$ varies with the position of the pointer and depends also on its length, which, for a specimen of fixed length, changes when the aperture is changed.

The scale angle, $A$, is only a part of the angle through which the specimen curls. The curling takes place in the part of the specimen that is wet, defined by the length of arc, $L$. The total angular displacement is $G=F+A-E$.

These factors are relatively unimportant in determining the time required to attain the maximum curl, for which the instrument was designed, but it seems necessary to consider them when a measurement of the amount of curl is the objective. Furthermore, the curl range is so great that it is not possible to obtain definite scale readings for all kinds of papers without changing the aperture setting. Unless the aperture setting is held constant, the scale angle alone is certainly not an acceptable measure of the relative degree of curl of different papers.

There are some other sources of uncertainty that have a tendency to make angle $A$ (fig. 1) too small. The curling is retarded by the cohesion of the water and the wet paper. Both the weight of the water lifted by the curling paper and the surface tension of the increasing liquid surface contribute toward this restraint to curling. The weight of the overhanging paper that serves as a pointer contributes further toward making angle $A$ smaller than it would be if the curling were unrestrained. The more pliable papers are more susceptible to these sources of error than the stiffer ones. Papers which curl slowly through a large angle may become partially dried out above the water line, a circumstance which contributes still further toward making the scale angle too small. Some of these limitations were discussed in a previous publication.[3]

The use of the flotation principle in determining the degree of curl of paper seems, nevertheless, not unreasonable. Since curling results from differential expansion, wetting one side intensifies the effect. The usual manner of making the test does, however, engender some doubt. It was thought possible to improve the test by modifying the procedure or by developing apparatus better adapted to the purpose, in order to minimize the various sources of uncertainty.

[3] Paper Ind. & Paper World **22**, 246 (June 1940).

## III. MAXIMUM CURVATURE AS A MEASURE OF CURLINESS

The curvature (reciprocal of radius of curvature), which takes into account the length of the wet portion of the paper, as well as the whole of the angle through which it curls, is a more comprehensive measure of the curl than is the scale angle. Therefore, if the maximum curvature of freely curling paper, unrestrained by the inhibiting influences that have been mentioned, could be determined, such a measure of relative curliness should be reasonably free of the uncertainties that characterize the present method. If proper allowance could be made for the restraining influences in the present method, one might make a fairly good estimate of the maximum curvature of freely curling paper from data obtained with the curl sizing tester. Both of these possibilities have been investigated.

### 1. NEW APPARATUS TO MEASURE CURVATURE

In view of the foregoing discussion, there appear to be two general ways in which the apparatus and procedure might be improved. The restraints to curling might be minimized so that moisture effects alone would be responsible for the curling. The measurement in terms of curvature could be facilitated. Several forms of apparatus were designed to achieve one or both of these ends. One of them is described below.

The restraints to curling can be greatly reduced by eliminating the paper pointer and by making the wetted length small so that the paper never lifts far from the general level of the water surface. The problem then is one of devising means sensitive enough to measure the curl with sufficient accuracy. Figure 2 is a sketch showing the principle of the method and of the apparatus used. The wetted length, $L$, is of course much exaggerated. One edge of the specimen is clamped at the water level, at $K$. A pivoted lever, having this clamping line as its axis of rotation, has an index registering on the scale and carries a hairline, $Q$, that is rotated, while the paper is curling, in such a manner as to keep it coincident with the chord of

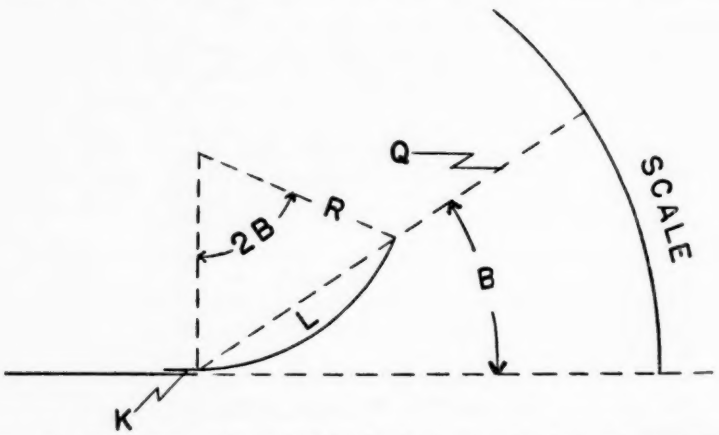


FIGURE 2.—*Sketch illustrating principle of optical apparatus devised to approximate free curling of paper when wet with water on one face.*

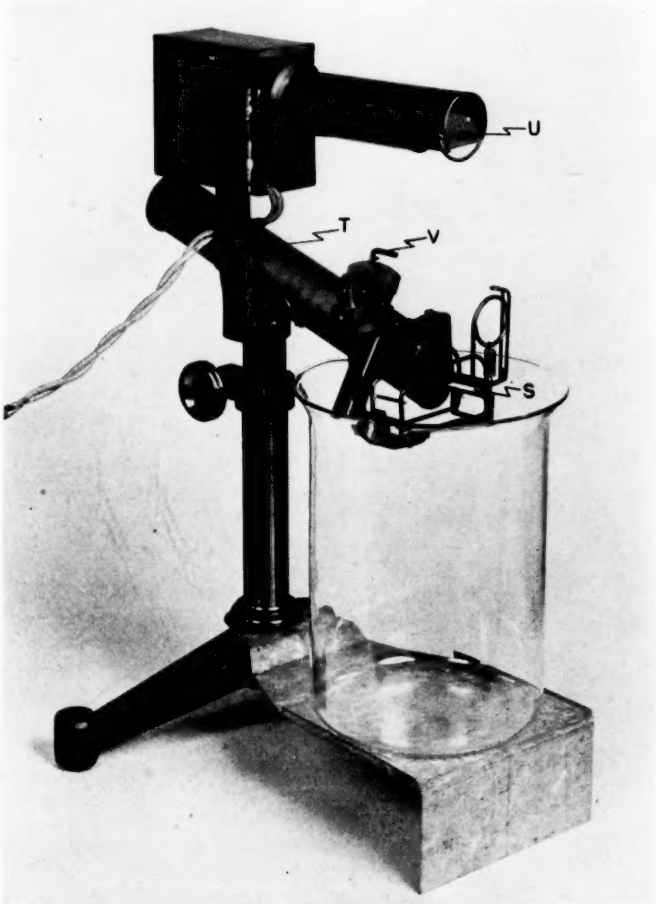


FIGURE 3.—*Optical apparatus for measuring degree of curl.*

arc $L$. The profile of the specimen is magnified to facilitate this adjustment. When the specimen has attained its maximum curl, the angle $B$ is read on the scale. The curvature is $2B/L$.

Figure 3 shows the apparatus, with which it is possible to measure $B$ when $L$ is only 3 or 4 mm in length. The narrow specimen, $S$, is seen through a low-power microscope, $T$. Light from the lamphouse above passes through a slit and is reflected from a mirror in the end of the tube, $U$, producing a sharp slit image across the specimen perpendicular to the axis of curl. A hairline ($Q$, fig. 2) in the microscope is rotated by the lever, $V$, (fig. 3) about the pivotal point, which appears to coincide with the point of intersection of an edge of the light slit with the clamping line (at $K$, fig. 2). As the paper curls, the image of the slit delineates the vertical profile of the specimen, and appears in the microscope as an upcurling arc. The hairline is rotated (in a plane parallel to that of the slit-image profile) by means of the lever, $V$, so that it appears as the chord of this arc. Hence, the position of the lever on the scale indicates angle $B$ of figure 2.

This optical apparatus, with the chief sources of uncertainty removed or considerably minimized, seems to give very good results, although they are not entirely independent of the arc length. The smaller lengths yield somewhat greater values of curvature. Of the several new instruments devised, the optical apparatus is the most complicated, and is perhaps the least convenient to use. Its continued use is rather fatiguing to the operator. Nevertheless, the tests made with various devices developed for applying the flotation principle to measuring degree of curl indicate that the optical apparatus gives the most reliable and reasonable results. It can therefore serve as a means of evaluating the curl sizing tester when used to determine the relative curling tendency of papers.

## 2. ESTIMATE OF CURVATURE WITH CURL SIZING TESTER

If tests made with the curl sizing tester in terms of the scale angle, $A$ (fig. 1), have been found useful in predicting curling tendency, an evaluation of curvature from similar data should be more valuable. If found to agree, or if they could be made to agree, with corresponding determinations made with the optical apparatus, such data should lend substantial support to the use of the curl sizing tester for determining the curling tendency of paper.

Although angle $A$ is not sufficient to determine the curvature of the curled specimen, an approximate value of curvature can be obtained if the wetted length, $L$, is also known. Arc $L$ is assumed to be the arc of a circle, since the expansion of the paper is substantially uniform. From the geometry of figure 1 it is apparent that the actual curvature of the specimen is given by the expression $G/L=(F+A-E)/L$. Since angle $A$ is read in degrees on the scale, it is convenient to express the curvature as degrees per centimeter of arc. Angle $F$ is a fixed angle of about 30 degrees. Angle $E$ is variable, but never large. An average value of 5 degrees could be assigned to it without introducing much error. Hence, the actual curvature, $G/L$, in degrees per unit length of arc, is approximately $(A°+25°)/L$.

The curvature of a freely curling specimen would be greater, however. Since angle $G$ is too small, because of the influences tending to restrain the curling, an increment, $D$, must be added. This in-

crement may be different for different papers. The curvature of a freely curling specimen therefore becomes $(G+D)/L$. An independent method of determining the curvature of freely curling paper, such as is afforded by the optical apparatus, would allow one to evaluate $D$ for various papers, and to formulate a provisional expression that could be used in calculating curvature from data obtained with the curl sizing tester, provided that $D$ does not vary too much. A modified procedure for the use of the curl sizing tester will materially facilitate the formulation. This special procedure is designed to make the wetted length small enough to reduce to some extent the restraints to curling on water, and yet yield a scale reading large enough to be read with sufficient accuracy. In this special procedure the aperture length[4] is made 1.2 cm, except that when the scale reading falls below 25 degrees the aperture length, $L$, is increased to a value such that angle $A$ (fig. 1) at maximum curl lies between 25 and 35 degrees. This procedure has the effect also of reducing the range over which $G$ (and presumably also that of $D$) will vary.

### 3. CURL DATA ON LITHOGRAPHIC PAPERS

Measurements of curl were made on a number of papers by means of the optical apparatus and the curl sizing tester, the special procedure being used. These measurements were made on 54 lithographic paperes which had been used in a research project[5] to improve the performance of lithographic papers in the printing process. These papers were made in the Bureau's experimental paper mill with variations in the beating treatment, which produced papers differing greatly in degree of curl.

The value of the increment, $D$, can be evaluated for each paper by setting the best available value of curvature, $K_0$, obtained with the optical apparatus, equal to $(G+D)/L$, the curvature formulated for the curl sizing tester, and solving for $D$. This was done for the 54 lithographic papers. An average value of 40 was thus found for $D$. A trial formula for the curvature, $K_s$, of freely curling paper, determined by means of the curl sizing tester, is therefore obtained by substituting 40 for $D$. That is, $K_s=(G+40)/L$, in which $G$ is approximately $A°+25°$. Values of $K_s$ were obtained for all of the 54 lithographic papers, and were compared with the corresponding values of $K_0$. All $K_s$ values were within 10 percent of the $K_0$ values, except for a very few that differed by 15 to 20 percent. The average difference was 6 percent. Table 1 is a condensation of typical data on approximately one-fourth of the papers, covering the range of curliness shown by these papers. In addition to the two sets of values of curvature, $K_s$ and $K_0$, the table also shows under $A_2$ the values obtained for the scale angle when a constant aperture length of a little more than 2 cm was used. These $A_2$ values represent the customary measure of relative curling tendency obtained with the curl sizing tester. The values for all three sets of measurements are plotted in figure 4. Data for some other pertinent properties[6] are also shown.

[4] The shorter, adjustable dimension of the aperture is designated in this paper as the length of the aperture, because it corresponds in direction to the length of the specimen, and is the length of the arc of the curved specimen in an apparatus such as that illustrated by figure 1.

[5] J. Research NBS **28**, 241 (1942) RP1455.

[6] The values for expansivity, sheet shrinkage, and density were made available by C. G. Weber, of the Bureau staff, whose many helpful suggestions during the investigation and in the preparation of the report the authors gratefully acknowledge. The values for curl time represent the data which the curl sizing tester was originally designed to obtain.

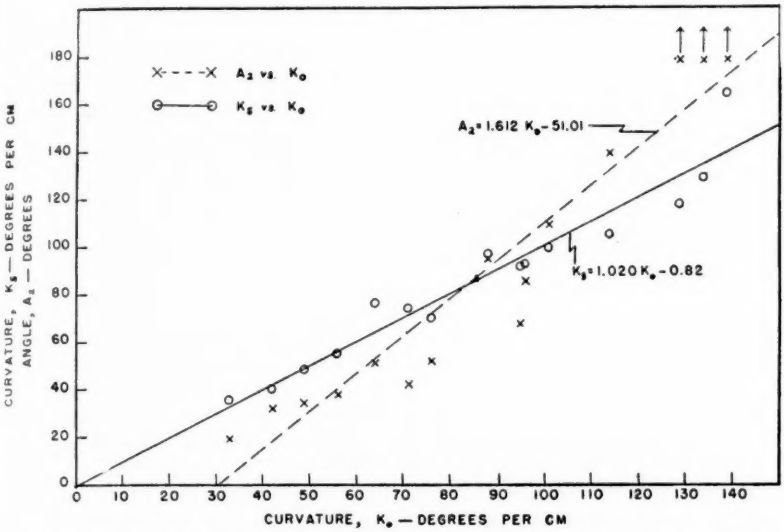


FIGURE 4.—*Degree of curl determined with the curl sizing tester in comparison with that determined with the optical apparatus.*

For meaning of symbols, see table 1, note 1. The equations of the best fitting straight lines were determined by the method of least squares.

TABLE 1.—*Curling and expansion data for a number of typical papers*

| Paper | Degree of curl [1] | | | Expansivity [2] cross direction | Sheet shrinkage, cross direction | Density | Air permeability [3] | Curl time |
|---|---|---|---|---|---|---|---|---|
| | $K_s$ | $K_0$ | $A_2$ | | | | | |
| | *deg/cm* | *deg/cm* | *deg* | *Percent* | *Percent* | *g/cm³* | *csm* | *sec* |
| 1 | 35 | 33 | 19 | 0.13 | 0.9 | 0.60 | 4,010 | 23 |
| 2 | 40 | 42 | 32 | .14 | 1.3 | .63 | 2,260 | 20 |
| 3 | 48 | 49 | 35 | .15 | 1.6 | .70 | 1,440 | 15 |
| 4 | 55 | 56 | 38 | .16 | 1.6 | .71 | 935 | 14 |
| 5 | 70 | 76 | 52 | .17 | 1.9 | .76 | 1,240 | 13 |
| 6 | 74 | 71 | 42 | .22 | 2.2 | .71 | 1,000 | 11 |
| 7 | 76 | 64 | 51 | .18 | 1.9 | .71 | 845 | 16 |
| 8 | 92 | 95 | 68 | .18 | 2.2 | .87 | 76 | 5 |
| 9 | 93 | 96 | 86 | .21 | 3.4 | .85 | 119 | 17 |
| 10 | 97 | 88 | 96 | .26 | 3.1 | .79 | 232 | 30 |
| 11 | 100 | 101 | 110 | .24 | 3.8 | .82 | 67 | 23 |
| 12 | 106 | 114 | 140 | .29 | 3.4 | .81 | 134 | 17 |
| 13 | 119 | 129 | 180+ | .31 | 4.4 | .80 | 39 | 28 |
| 14 | 130 | 134 | 180+ | .31 | 3.8 | .87 | 99 | 17 |
| 15 | 166 | 139 | 180+ | .32 | 5.6 | .85 | 25 | 34 |
| CORRELATION [4] | | | | | | | | |
| $r$ | 0.97 | 0.9 | 0.91 | 0.95 | 0.85 | −0.77 | 0.45 | |
| $k$ | .90 | .9 | .92 | .92 | .70 | −.79 | .30 | |

[1] $K_s$=curvature from data obtained with curl sizing tester and special procedure; $K_0$=curvature from data obtained with optical curl tester; $A_2$=scale reading (angle) on curl sizing tester with fixed aperture length of about 2.2 cm.

[2] For a change of 15 percent in relative humidity.

[3] The unit csm = cubic centimeters of air flowing per second through a square meter of paper under unit-pressure difference (1 g/cm²).

[4] The Pearson correlation coefficient, $r$, is calculated as $\Sigma xy/\sqrt{\Sigma x^2 \Sigma y^2}$, in which $x$ is the difference between the mean value and any value of $K_s$ in the table, and $y$ is the difference between the mean value and any value of the property whose correlation with $K_s$ is being determined.

The Kendall (Biometrika **30**, 81 (1938)) coefficient of rank correlation, $k$, with $K_s$ is determined by arranging the papers in the order of increasing values of $K_s$ and calculating $k$ for each of the other properties as $1-4Ss/[n(n-1)]$, in which $n$ is the number of items (papers), $s$ is the number of items following a given item which have values *smaller* than the given item, and $\Sigma s$ is the sum of the $s$ values for all of the $n$ items.

## IV. DISCUSSION OF CURL MEASUREMENT

It is improbable that any one test could be devised that would evaluate the relative curling tendency of papers for all conditions of use. Papers may be completely and evenly exposed to the atmosphere, or they may be partially and unevenly exposed. Some papers are far less uniform in structure than others. If a paper is "two-sided," that is, if the two faces differ sufficiently in structure and character (a frequent occurrence in machine-made papers), free exposure to a new hygrometric condition is likely to result in unequal contraction or expansion of the two surfaces. The result is curling. A more nearly homogeneous paper, which might not curl under these conditions, would be more likely to do so if exposed in such manner that one surface is partly covered, or if for any reason there is brought about a nonuniform absorption or distribution of moisture in the sheet. Much depends also on the moisture-content history of different papers. The ability to predict the relative curl of two or more papers in use involves, moreover, the tacit assumption that the papers will be stored and used under similar hygrometric conditions. Curling may also be associated with a strained condition in the paper acquired during fabrication, and it may be influenced by mere position, the stiffness having an important bearing on relative behavior.

Considering the complexity of factors entering into the curling of paper, the data presented indicate that the curl sizing tester affords a measure of curliness that is probably good enough for most practical requirements, particularly if the procedure here recommended is used. If one is interested only in the relative rank of a set of papers, the customary measurement of the angle alone ($A_2$ of table 1) on the scale of the curl sizing tester, when a given aperture setting is used, may serve the purpose. The scale of values, however, will be distorted. If the group of papers includes extremes, such that the very curly ones go beyond the limit of the scale (as in the case of the last three values under $A_2$ of table 1), this measure will not be adequate even for ranking. A better balanced and more useful measure can be obtained with little additional effort, however, in terms of the maximum curvature. The data in table 1 and figure 4 indicate that the curvature values obtained with the curl sizing tester, used according to the special procedure, agree well with those obtained with the optical apparatus, which gives the nearest approach to freely curling paper that we have been able to achieve in a flotation test.

The investigation began with the assumption that the curl sizing tester would prove to be so poorly adapted to measuring degree of curl that a better instrument could easily be devised. But, on the basis of the data obtained, the best apparatus we were able to devise to apply the flotation principle is so little superior to the curl sizing tester, when used according to the recommended procedure, that its use to displace the curl sizing tester as a means of measuring degree of curl does not seem to be justified. The curl sizing tester, moreover, is a simpler and more practical instrument, and is already widely available.

Since the curling of paper is the result of differential expansion, and since there is usually some degree of "two-sidedness," either in the paper or in the conditions of exposure, a paper that is susceptible to

expansion is more likely to curl than one which suffers little dimensional change with changes in moisture conditions. One is therefore led to expect some correlation of the test with expansivity and with other properties associated with expansivity. Table 1 shows fairly good correlation of the degree of curl with expansivity, shrinkage during fabrication, density, and air permeability. Density and air permeability are related to expansivity, in that a dense, relatively impermeable sheet usually means "hydration" and bonding of contiguous fibers that make the sheet expand or contract as a unit, whereas in a bulky, loosely bonded, permeable sheet the fibers move more with respect to one another when they swell or shrink, and less sheet movement results.

No evidence has been presented so far to show that the tests made are actually useful in predicting the curling tendency of paper under service conditions. Data of this character are hard to obtain, but such comparisons as it has been possible to make between the curvature determined in the flotation test and curling tendency in use, or under simulated service conditions, have been very gratifying.

The papers listed in table 1 were observed under a condition favorable to curling that is frequently encountered in use—sudden exposure to dry air. The papers were first conditioned at 50-percent relative humidity and then transferred to a dry atmosphere (about 12-percent relative humidity). Except for two papers, 11 and 14, the departure from flatness of the horizontally supported sheets correlated very well with the curvature, $K_s$, determined with the curl sizing tester, the rank correlation, $k$, for the others being 0.85 to 0.90.

A similar comparison was made of independent measurements on 11 papers submitted by a commercial firm. This firm first ranked the papers according to their observation of the behavior of the papers when transferred from an atmosphere of 35-percent relative humidity to very dry air, giving values for change in curvature. The same papers were tested at the Bureau with the curl sizing tester, values of $K_s$ being obtained for the comparison. The correlation was again satisfactory, the Pearson correlation coefficient being 0.8.

An opportunity was had to observe the curling of six of the papers listed in table 1 (papers 1, 5, 6, 10, 14, and 15) while being printed in five colors by the offset process under identical conditions and with like moisture conditioning. Paper 1, with the lowest degree of curl, measured with the curl sizing tester (table 1), remained flat at all times. Papers 5 and 6 curled slightly during the first printing. Number 10 showed a definite tendency to curl. Numbers 14 and 15 curled so much that they interfered with the operation of the automatic feeders.

WASHINGTON, November 19, 1942.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1523

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# COMBINATION OF WOOL PROTEIN WITH WEAK ACIDS

By Jacinto Steinhardt, Charles H. Fugitt, and Milton Harris[1]

ABSTRACT

Previous studies of the combination of wool with strong acids have been extended to include 13 weak acids. It is shown that, unlike strong acids, these substances combine with wool in the molecular (undissociated) as well as in the ionic (dissociated) form. The amounts combined as molecules may far exceed the amounts taken up as ions.

Estimates are given of the relative tendencies of these weak acids to combine with wool. They vary over a three-hundredfold range. The negligible effect of temperature on the equilibrium between wool and one of these acids, monochloroacetic, suggests that the combination with undissociated acids is akin to a competitive solvation and involves the displacement of combined water.

CONTENTS

| | Page |
|---|---|
| I. Introduction | 123 |
| II. Experimental procedure | 124 |
| III. Results and discussion | 124 |
| IV. References | 128 |

## I. INTRODUCTION

Numerous studies have been made of the combination of wool with acids and bases [1, 2, 3, 4, 5, 6].[2] With the notable exception of some measurements by Speakman and Stott [1], practically all of these studies have been made with strong acids and bases which are totally dissociated into their constituent ions. Thus, little is known of the effect of the presence of undissociated acids on the equilibrium between wool and hydrogen ions, or of the relative affinities for wool of the anions of various weak acids. Such knowledge is of practical interest because wool is often exposed, in processing, to solutions which contain weak acids, such as acetic, formic, or glycolic.

It is the purpose of the present paper to show the extent to which wool combines with a number of weak acids, and to demonstrate that wool combines not only with the ions of these acids but with molecules of the undissociated acid as well. The very large extent of combination with wool of such weak acids as formic acid and monochloroacetic acid, in the undissociated form, acquires particular significance in view of the long-known profound influence of these substances on the dyeing, swelling, and the stress-strain characteristics of wool fibers [1]. Similar combination with undissociated acid by dissolved proteins has recently been reported [7].

[1] Research Associates at the National Bureau of Standards, representing the Textile Foundation.
[2] Figures in brackets indicate the literature references at the end of this paper.

## II. EXPERIMENTAL PROCEDURE

Details of the purification of the wool, of the determination of the acid combined, and of the pH have been described elsewhere [3, 4]. Except where otherwise noted, all the reagents used were of reagent grade, and were used without further purification, except for the removal of traces of strong acids present as impurities. Glycolic acid was treated with barium hydroxide to remove sulfuric acid. Hydrochloric acid was removed from solutions of dichloroacetic acid by silver oxide. The phenolic derivatives and nicotinic acid were recrystallized from hot water from one to four times. With one exception, all the experiments were made at 0° C.

## III. RESULTS AND DISCUSSION

The results obtained with most of the weak acids used are compared in figure 1 with those previously obtained with one strong acid, hydrochloric [3]. This graphic comparison brings out clearly the principal difference between the behavior of strong and weak acids with respect to wool. Over a wide range of low concentrations, many of the acids are combined by wool at a given pH to about the extent that it combines with hydrochloric acid. The presence of undissociated acid at these concentrations is without appreciable effect. At higher concentrations, however, the amounts of weak acids which are combined increase more sharply than the amounts combined of hydrochloric acid, and, unlike the latter, give no indication of approaching a saturation value at about 0.8 millimole per gram. Indeed, determinations have been made of amounts combined which are far beyond the upper limits of figure 1 (up to 4 millimoles/g).

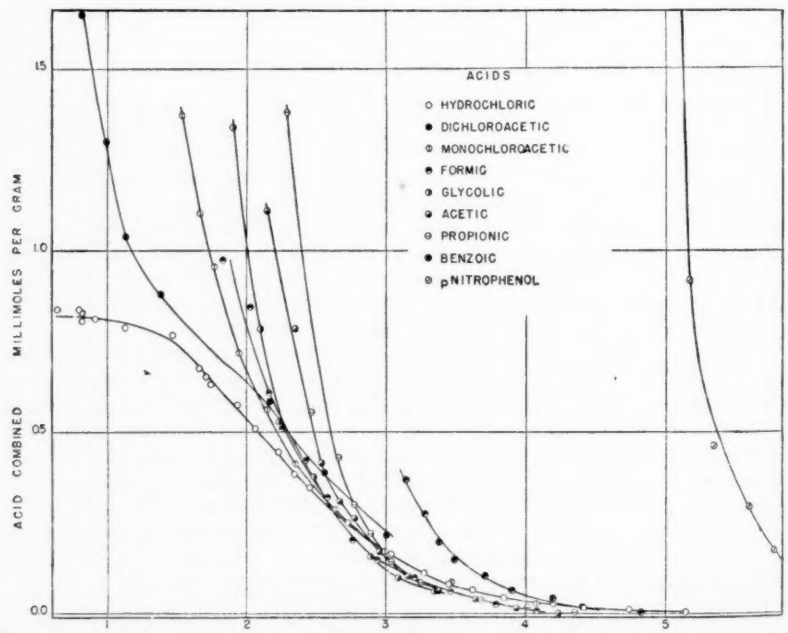


**Figure 1.**—*Combination of purified wool with a number of weak acids at 0° C.*
The curve for hydrochloric acid is given for comparison.

It has been shown in earlier papers that different strong acids at the same concentration combine with wool to different extents [5, 6]. Most of the acids shown in figure 1 are organic acids of relatively low molecular weight, and would be expected, if totally dissociated, to give titration curves of wool similar to that obtained with hydrochloric acid [6]. If attention is confined to the lower portion of the curves obtained with acids of molecular weights below 80, it appears that this expectation is well founded. Marked departures from the curve for hydrochloric acid appear only at concentrations at which the amounts of undissociated acid become greater than about 0.01 *M*.

It may be shown that the increased uptake of weak acids which appears at high concentrations is a rough measure of the amounts of *undissociated acid* that have combined with the wool, possibly by solvating it in competition with water. This demonstration depends on the two experimental results described below: First, this increased uptake of any weak acid is approximately proportional to the concentration of undissociated acid. Second, the increased uptake of any one acid at a given pH value is not fixed, but varies with the concentration of the weak acid.[3]

The first of these generalizations has been tested with the data for all the carboxylic acids studied, with fairly satisfactory results. A representative set of calculations is reproduced in table 1. Monochloroacetic acid has been chosen as an example because the lower part of the curve of this acid coincides most closely with that for hydrochloric acid. Since this coincidence implies that the two acids, when dissociated, have closely similar affinities for wool, this acid should be most suitable for an application of the test. As the table shows, over more than a fiftyfold range of concentration of acid, the proportionality between the extra uptake and the concentration of acid varies by less than half of its mean value, a satisfactory result in view of the assumptions underlying the calculations. The factor of proportionality, which hereafter will be referred to as the partition coefficient, shows a pronounced tendency to fall as the amounts combined increase. This must be expected, whatever view of combination is postulated, since the amounts combined must approach an upper limit unless the fibers swell indefinitely and dissolve. The upper limit indicated by the results, however, must lie far above the highest experimental values shown in the tables. Thus, little purpose would be served by attempting to evaluate it by extrapolation,[4] since the accuracy of the titration data is lower at high concentrations of acid, where only a small fraction combines, and the effects of water absorption by the fibers are greatest [3, 4].[5]

The values of the quotient (column 7, table 1) at the highest dilution should come closest to expressing the inherent tendency of the acid to combine with or to solvate wool. However, it must be recognized that it is these values which are most subject to error. They

[3] The concentration of weak acid may be varied, while the pH is held constant, by adding a strong base in such proportion that the ratio of dissociated acid: undissociated acid remains unchanged.

[4] The upper limit of the amounts combined may be fixed either by a stoichiometric limit, that is, the replacement by acid of all the combined water, or by the development of a definite swelling pressure within an elastic structure due to the difference between the molecular volumes of each acid and water. A decision between these alternatives requires accurate estimates of the maximum amounts of combination of different acids having widely different molecular volumes.

[5] Efforts have been made to estimate the latter effect by comparing the results of the experiments with dry wool fibers with the results obtained with fibers containing 14 percent of moisture. These experiments indicate that the uptake of acid for the first three entries in table 1 may be as much as 10, 6, and 3 percent higher than the values given. The quotients in the last column are correspondingly affected with a resulting improvement in constancy.

TABLE 1.—*Combination of undissociated monochloroacetic acid with wool at 0° C*

| pH | Acid combined [1] | HCl combined at same pH | Difference | Total acid | Undissociated acid [2] | Excess combination divided by concentration of undissociated acid |
|---|---|---|---|---|---|---|
| | *mmoles/g* | *mmoles/g* | *mmoles/g* | *mmoles/liter* | *mmoles/liter* | |
| 1.36 | 2.08 | 0.79 | 1.29 | 0.971 | 0.937 | 1.4 |
| 1.52 | 1.39 | .77 | .62 | .477 | .455 | 1.4 |
| 1.66 | 1.12 | .71 | .41 | .282 | .265 | 1.5 |
| 1.76 | 097 | .66 | .31 | .184 | .070 | 1.8 |
| 1.95 | .73 | .59 | .14 | .0874 | .0769 | 1.8 |
| 2.15 | .580 | .504 | .076 | .0398 | .0332 | 2.3 |
| 2.35 | .431 | .403 | .028 | .0172 | .0132 | 2.1 |

[1] No corrections have been applied for the error in calculating the uptake of acid which is introduced by the absorption of water by the fibers. See footnote 6, page .

[2] The values in this column are derived from the total acid present by utilizing Wright's value of the dissociation constant [8], and applying the law of mass-action. Since the proportion ionized is small, except in the more dilute solutions, little error is introduced by the neglect of activity coefficients.

depend on the estimation of very small differences between the ordinates of the curves for monochloroacetic acid and for hydrochloric acid, and are also affected most strongly by any failure of the assumption that the anions of these two acids have the same affinity for wool.

The second generalization results from experiments made with monochloroacetic acid over the same range of pH values but at higher concentrations of undissociated acid. This was accomplished by having a constant amount (0.2 *M*) of potassium monochloroacetate in all the solutions. The results of these experiments are shown in table 2. Here the data for hydrochloric acid which are subtracted are not the same as those used in table 1. Instead, values previously reported for the combination of hydrochloric acid in the presence of 0.2 *M* potassium chloride have been used. Again, the quotients entered in column 7 of table 2 are not constant, but show a trend. They agree fairly closely with the values of the quotients shown in the first table for similar concentrations of acid, but the spread is larger because higher concentrations of acid were used.[6] In keeping with the higher concentrations, very much larger

TABLE 2.—*Combination of undissociated monochloroacetic acid with wool, in the presence of 0.2 M potassium monochloroacetate at 0° C*

| pH | Acid combined [1] | HCl combined at same pH | Difference | Total acid | Undissociated acid | Partition quotient |
|---|---|---|---|---|---|---|
| | *mmoles/g* | *mmoles/g* | *mmoles/g* | *mmoles/g* | | |
| 1.59 | 3.29 | 0.79 | 2.50 | 2.46 | 2.43 | 1.0 |
| 1.76 | 2.67 | .78 | 1.89 | 1.73 | 1.71 | 1.1 |
| 1.93 | 2.31 | .77 | 1.54 | 1.21 | 1.20 | 1.3 |
| 2.07 | 2.04 | .75 | 1.29 | 0.885 | 0.876 | 1.5 |
| 2.23 | 1.66 | .74 | 0.92 | .594 | .588 | 1.6 |
| 2.53 | 1.17 | .70 | .47 | .299 | .296 | 1.6 |
| 2.86 | 0.90 | .62 | .28 | .143 | .142 | 2.0 |
| 3.20 | .72 | .55 | .17 | .067 | .067 | 2.5 |

[1] No corrections have been applied for the error in calculating the uptake of acid which is introduced by the absorption of water by the fibers. See footnote 6. The values in this column are calculated by subtracting the antilogarithm of the pH from the value in the preceding column.

[6] Corrections for the effects of water absorption by the fibers in this experiment would be higher than in the preceding experiment and would serve to reduce the spread.

amounts of acid are here combined, in the same range of pH which was covered in the experiment without potassium chloride. Thus the amounts of monochloroacetic acid taken up in excess of the amounts of hydrochloric acid taken up at the same pH values have been shown in two different kinds of experiments to be proportional to the amounts of undissociated acid. It thus appears very likely that the excess uptake of acid is in the undissociated form.

The experiments just described show clearly that in evaluating the relative tendency of the weak acids represented in figure 1 to combine with wool, little consideration should be given to the pH range at which combination occurs. Thus it appears from the figure that acetic acid is taken up at lower acidities than chloroacetic acid. This depends entirely upon the fact that acetic acid is much the weaker of the two acids, and does not signify, as it would have in the work with strong acids, that acetate has a higher affinity than monochloroacetate. Since the acid taken up is largely in the undissociated form, it is the concentration of acid rather than the hydrogen ion present, which is significant. At equal concentrations of these two acids, considerably more monochloroacetic acid is taken up than acetic acid. It seems reasonable to interpret this combination with *undissociated acids* as a solvation, which depends on the fact that the acids are hydroxylic compounds rather than on their nature as acids.

The inherent tendencies of the acids examined to combine with wool in their undissociated form have been calculated by the method shown in table 1. To avoid inconsistencies which might arise from trends in the quotients, the values corresponding to the same extent of combination, 0.2 to 0.3 millimole of undissociated acid per gram of wool, have been tabulated. The results are summarized in table 3. Approximate values for a few cyclic compounds not represented in figure 1 are also included. The range of the affinities of the undissociated acid for wool, as shown in the table, is approximately 300 to 1.

TABLE 3.—*Relative affinities of undissociated acids for wool protein at 0° C.*

| Acid | Partition quotient |
|---|---|
| Propionic | 0.3 |
| Acetic | 0.4 |
| Glycolic | 0.6 |
| Formic | 0.7 |
| Nicotinic | [a] 1.5 |
| Monochloroacetic | 1.8 |
| Dichloroacetic | 2 |
| Benzoic | 11 |
| *p*-Nitrophenol | 20 |
| 2,4-Dinitrophenol | 50 |
| 2,6-Dinitrophenol | 60 |
| 2,6-Dichloro-4-nitrophenol | 100 |
| 2,4,6-Trichlorophenol | 100 |

[a] The low value for nicotinic acid is probably due to the use of an incorrect value for the concentration o undissociated acid. It appears probable that a large proportion of the acid is in the zwitterionic form. Due to the high degree of ionization of this acid, the value given is an approximation.

Estimates are available of the heats of combination of a number of strong acids with wool [4, 6]. Values between 2,000 and 12,000 calories have been obtained, the higher values being characteristic of the acids of high affinity. An effort has been made to obtain similar

heat data for the combination of monochloroacetic acid *in the undissociated form.* This acid has again been selected, partly for the reasons already given and partly because Speakman and Stott [2] have determined by a calorimetric method the heat liberated in its combination with wool. In the present study an estimate of the heat of combination has been made by comparing the partition coefficient at two different temperatures, 0° and 25° C.

Experiments with monochloroacetic acid at 25° C yielded partition coefficients practically the same (within the experimental error) as those given in table 1. If it is assumed that a difference of as much as 10 percent in the partition coefficient would have been detected, it follows from the Van't Hoff equation that the heat absorbed in the combination of the undissociated acid by wool is at most only 300 or 400 calories per mole of acid [4]. This value is so close to zero that it supports the view that the combination with undissociated acid involves the replacement of another hydroxylic compound, presumably water, i. e., a process of selective solvation. The heat of hydration of wool and other proteins is large, but the replacement of 1 solvated molecule by another which is held only slightly more strongly, would probably involve only very small heat changes, such as are found here.[7]

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WASHINGTON, November 23, 1942.

[7] The heats of combination with wool of monochloroacetic acid, given by Speakman and Stott, are averages of the heats of both the ionic and the nonionic reactions, and are therefore higher than those indicated here. It has already been pointed out [4] that the trends in the values given by these authors indicate a very low heat of reaction for amounts combined in excess of 0.8 millimole per gram.

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# H VALUES OF CERTAIN PHOSPHATE-CHLORIDE MIXTURES, AND THE SECOND DISSOCIATION CONSTANT OF PHOSPHORIC ACID FROM 0° TO 60° C

By Roger G. Bates and S. F. Acree

ABSTRACT

Measurements of the electromotive forces of galvanic cells composed of hydrogen and silver–silver-chloride electrodes in aqueous chloride-phosphate solutions were made at 5-degree intervals from 0° to 60° C. The solutions were mixtures of sodium chloride, disodium hydrogen phosphate, and either sodium or potassium dihydrogen phosphate; three ratios of the molalities of the two phosphate salts were employed, and a wide range of concentrations was covered. The second dissociation constant was evaluated from the experimental data. The values of the negative logarithm of the constant at each of the 13 temperatures studied may be computed from the following equation:

$$pK_2 = 1979.5/T - 5.3541 + 0.019840T,$$

where $T$ is in degrees Kelvin.

For each temperature, the heat and entropy of dissociation, the change of heat capacity, and the free-energy change accompanying the dissociation of 1 mole of $H_2PO_4^-$ were computed from the variation of the second dissociation constant with temperature.

The pH value of each solution was calculated. The pH values from 0° to 60° C of mixtures of sodium (or potassium) dihydrogen phosphate, disodium hydrogen phosphate, and sodium chloride, in which $m_{H_2PO_4} = m_{Cl}$ and the ratio of the molality of $H_2PO_4^-$ to that of $HPO_4^=$ lies between 0.2 and 5.0, are given by the equation

$$(pH)_t = (pK_2)_t - \log (m_{H_2PO_4}/m_{HPO_4}) - 3A\sqrt{\mu}/(1 + Ba_i\sqrt{\mu}),$$

where $\mu$ is the ionic strength. These solutions are proposed as pH standards in the range 6.4 to 7.4.

CONTENTS

| | | Page |
|---|---|---|
| I. | Introduction | 130 |
| II. | Method | 130 |
| | 1. Dissociation of phosphoric acid in water | 130 |
| | 2. Dissociation constants from cells without liquid junction | 132 |
| | 3. pH values of the phosphate-chloride mixtures | 134 |
| III. | Errors of method and simplifications | 134 |
| | 1. Buffer ratio | 134 |
| | 2. Effect of carbonate | 135 |
| IV. | Experimental methods | 136 |
| | 1. Equipment | 136 |
| | 2. Materials | 137 |
| | 3. Solutions | 139 |
| | 4. Electrodes | 140 |
| | 5. Procedure | 140 |
| V. | Calculation of the dissociation constant | 141 |
| VI. | Thermodynamic quantities | 147 |
| VII. | pH values of phosphate solutions | 149 |
| VIII. | References | 154 |

## I. INTRODUCTION

In the preparation of many commercial products the rapidity and efficiency of the processes depend upon the accurate control of the acidity, or alkalinity, of aqueous solutions. Such control is now a regulatory requirement in certain medicinal preparations and in paper and leather manufactured for the Government. Among other applications, one of particular importance is the avoidance of corrosion and embrittlement of boiler walls and tubes by the control of the acidity of boiler water.

It is important to have recognized pH standards for the control of operations and products and for the calibration of the necessary laboratory and plant equipment, and several such standards have been proposed. The National Bureau of Standards is engaged in developing precise pH standards to cover the useful pH ranges and in making them available for scientific and industrial work. A list of standard buffers and their provisional pH values at 20°, 25°, and 30° C has recently been prepared [1].[1]

Buffer solutions prepared from anhydrous potassium dihydrogen phosphate ($KH_2PO_4$) and anhydrous disodium hydrogen phosphate ($Na_2HPO_4$) are among the most suitable standards for the pH range 6 to 8. Both substances are readily prepared in a state of high purity. Neither substance will take up moisture from an atmosphere whose relative humidity does not exceed 40 percent at 25° C. The pressure of water vapor in equilibrium with a system containing solid potassium dihydrogen phosphate and its saturated solution at this temperature is 22.76 mm (96-percent relative humidity) [2]. Anhydrous disodium hydrogen phosphate and the dihydrate are in equilibrium at 25° C with water vapor at a partial pressure of 9.80 mm (relative humidity of 41 percent) [3]. Absorbed moisture was readily lost when the salts were dried for 2 hours at 110° to 120° C.

The first step in the accurate determination of the pH values of mixtures of phosphate salts at several temperatures is the measurement of the ionization, or dissociation, constants of phosphoric acid. The second dissociation constant has been studied at 18° C by several investigators, by the use of cells with liquid junction. The earlier results varied widely. More recently, Bjerrum and Unmack [4] used cells with liquid junction at 18°, 25° and 37° C. Nims [5] extended the range of temperature and calculated the constant from measurements of cells without liquid junction at 5-degree intervals from 20° to 50° C.

It is the purpose of this paper to report a determination of the pH values of some phosphate solutions, the second dissociation constant of the acid, and related thermodynamic quantities, at 5-degree intervals from 0° to 60° C.

## II. METHOD

### 1. DISSOCIATION OF PHOSPHORIC ACID IN WATER

The distribution of hydrogen among the primary, secondary, and tertiary phosphate ions and the water is determined by the relative

[1] Figures in brackets indicate the literature references at the end of this paper.

amounts of these several species and by the magnitudes of the mass-action constants,[2] K, for the following equilibria:

$$H_3PO_4 = H^+ + H_2PO_4^- ; K_1. \quad (1)$$
$$H_2PO_4^- = H^+ + HPO_4^= ; K_2. \quad (2)$$
$$HPO_4^= = H^+ + PO_4^{\equiv} ; K_3. \quad (3)$$
$$H_2O = H^+ + OH^- ; K_w. \quad (4)$$

When a 0.1 *M* solution of phosphoric acid is titrated with 0.1 *M* alkali solution the titration curve [6] of figure 1 is obtained. In the

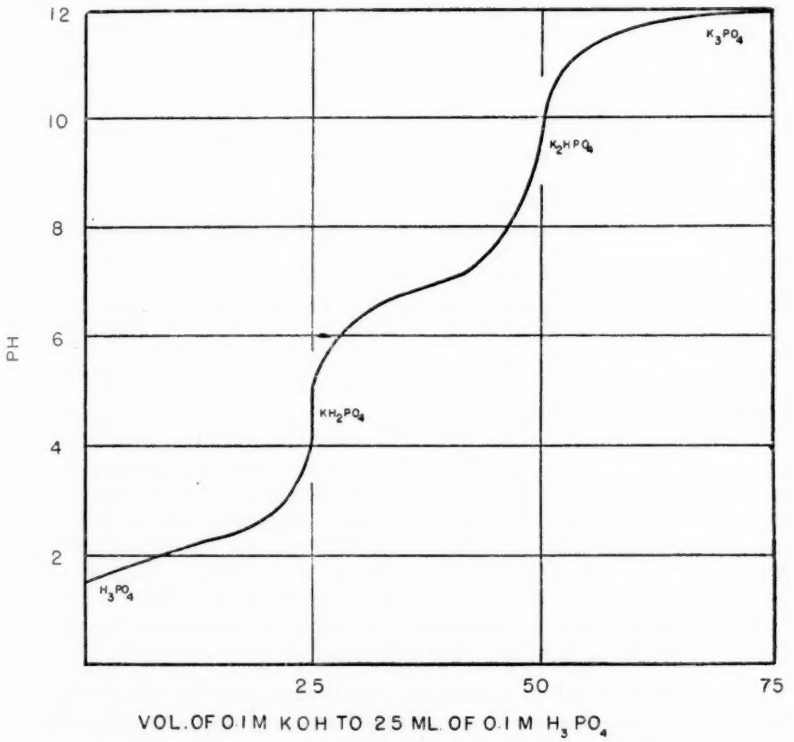


FIGURE 1.—pH *changes in the titration of a solution of phosphoric acid with strong alkali.*

region of the curve corresponding to the addition of 25 to 50 ml of the alkali to 25 ml of the acid, equilibrium 2 is the only one of significance. The solutions studied in determining the second dissociation constant have pH values which lie near the center of this region of the titration curve.

[2] This term may be applied correctly to any specified equilibrium. For equilibria of types 1 and 4, the term "ionization constant" may be employed. The use of this term for reactions 2 and 3, where ions are both reactants and products, is not as fortunate. The term "dissociation constant" will be applied here to all four of these equilibria. It is understood that each equilibrium should include water as a reactant:

$$HA + H_2O = H_3O^+ + A^-.$$

Water has been omitted for simplicity, and hydronium ion ($H_3O^+$) will be referred to as hydrogen ion ($H^+$).

## 2. DISSOCIATION CONSTANTS FROM CELLS WITHOUT LIQUID JUNCTION

If the dissociation of a weak acid mixed with one of its salts conformed to the simple law of mass action at useful concentrations, the dissociation constant of the acid could be obtained from electromotive force (emf, $E$) measurements of a single mixture. As a consequence of association, interionic or salt effects and other factors, such solutions depart from ideality as the concentration increases. It is therefore necessary to extrapolate the data to zero concentration to secure "ideal" constants freed from such disturbing effects [7, 8].

In the early studies of ionization by use of emf measurements, the contact between the reference half-cell (usually saturated potassium chloride, calomel) and the solution under investigation gave rise to an uncertain liquid-junction potential. Various attempts were made to increase the accuracy of the method by reducing the liquid-junction potential to small values and by the use of cells without liquid junction [9, 10, 11, 12].

More recently, Harned and coworkers have outlined a method [13, 14, 15] for obtaining dissociation constants of weak acids, bases, and ampholytes by thermodynamic procedure from measurements of galvanic cells without liquid junction.[3] In this method, hydrogen and silver-chloride electrodes are employed in buffered chloride mixtures. An extrapolation to infinite dilution yields the thermodynamic equilibrium constant.

The cell employed in this investigation may be represented by the following arrangement:

$$\mathrm{Pt|H_2|NaH_2PO_4\ or\ KH_2PO_4}\ (m_1),\ \mathrm{Na_2HPO_4}\ (m_2),\ \mathrm{NaCl}\ (m_3)\ \mathrm{|AgCl|Ag} \qquad (5)$$

where $m_1$, $m_2$, and $m_3$ are the molalities of the components of the solution in which the electrodes are immersed. Use is made of the silver–silver-chloride electrode because its standard potential has been determined [17] over the temperature range 0° to 60° C. The reproducibility of this electrode, prepared by three different procedures, is attested by the work of Smith and Taylor [18].

The total reaction for each faraday drawn reversibly from cell 5 is

$$1/2\mathrm{H_2(g,\ 1\ atm)+AgCl\ (s)=Ag\ (s)+H^+ + Cl^-}. \qquad (6)$$

The emf of the cell measures the tendency for reaction 6 to take place.[4] It is related to the activities [5] of the hydrogen and chloride ions by the Nernst equation in the form

$$E-E^\circ=-\frac{RT}{F}(2.3026)\log\ (a_{\mathrm{H}}a_{\mathrm{Cl}})=-\frac{RT}{F}(2.3026)\log\ (a_{\mathrm{H}}m_{\mathrm{Cl}}f_{\mathrm{Cl}}) \qquad (7)$$

[3] For the application of the method in this Bureau to the determination of the second dissociation constant of malonic acid, see the paper by Harner, Burton, and Acree [16]. The results of a recalculation of the standard potential of the silver-silver chloride electrode from recent values of the natural constants and the electromotive-force data of Harned and Ehlers [17] are also listed.

[4] The presence of unrecognized "side reactions" is responsible for a frequent error in emf measurements. In such cases, irreversible chemical reactions at either electrode effect a lowering of the measured emf or an elevation above the value which measures the tendency for the principal reaction of the cell to proceed. This type of polarization is known to be absent from hydrogen-silver-chloride cells when reasonable precautions are taken to prevent silver ion from diffusing to the hydrogen electrode, when substances reduced in solution by hydrogen are absent, and when oxygen is excluded. The residual liquid-junction potential caused by the solubility of silver chloride in the solutions is small at finite concentrations and disappears in the determination of the dissociation constant, since both $E^\circ$ and $K$ are obtained by an extrapolation to pure solvent.

[5] The activities of ions and molecules are usually represented by $a_i$ and $a_m$. By definition, $a_i=f_i m_i$, where $f_i$ is the activity coefficient of the ions of species $i$, the concentration, $m_i$, of which is expressed in moles (gram ions) per kilogram of water. The value of an activity coefficient depends on the scale of concentration used, and where it is necessary to make the distinction subscripts are added. Thus $f_m$, $f_c$, and $f_x$ represent, respectively, activity coefficients on the molal, volume concentration, and mole fraction scales. In this paper the molal scale is employed exclusively, and the subscript is omitted. The symbol $\gamma$ is often used for $f_m$.

where $R$ is the gas constant (8.3127 Int. j deg $^{-1}$ mole $^{-1}$ [19], $T$ is the absolute temperature ($t$+273.16) [20], $\boldsymbol{F}$ is the faraday (96,500 Int. coulombs [20]), and $E°$ is the standard potential of cell 5.

The equilibrium expression for the second dissociation of phosphoric acid (eq 2) is formulated as follows:

$$K_2 a_{H_2PO_4} = a_H a_{HPO_4} \tag{8}$$

or

$$K_2 m_{H_2PO_4} f_{H_2PO_4} = a_H m_{HPO_4} f_{HPO_4}, \tag{8a}$$

in which $K_2$ is the second dissociation constant. The symbol $\mathbf{a}_H$ represents the activity of the hydrogen ion and all of its solvates to which the hydrogen electrode is reversible. The negative common logarithm of this activity is the pH value. In contrast with the inadequacy of the simple mass-law expression, eq 8 and 8a are exact.

Since the hydrogen-ion activity in mixtures of primary and secondary phosphate ions in the pH range 5 to 9 is governed principally by eq 8a, combination of this expression with eq 7 gives a relation involving electromotive force, the second dissociation constant, activity coefficients, and the molalities of the buffer solutions used in the cells:

$$pK_2 = (E-E°)/k + \log(m_{H_2PO_4} m_{Cl}/m_{HPO_4}) + \log(f_{H_2PO_4} f_{Cl}/f_{HPO_4}), \tag{9}$$

where $pK_2$ is the negative logarithm of $K_2$ and $k$ is written for $2.3026RT/\boldsymbol{F}$.

If the activity coefficient of each ion species in the phosphate-chloride mixtures were known accurately, a single measurement of emf would suffice to determine the value of $pK_2$ at a particular temperature. Unfortunately, activity coefficients for mixtures such as these are not known with precision, and the solution of eq 9 is impossible. Likewise, the extremely dilute region in which the last term of the equation becomes negligibly small is experimentally inaccessible. Recourse may be had, however, to extrapolation formulas such as the Debye-Hückel limiting-law expression, $-\log f_i = Az_i^2\sqrt{\mu}$ [21], or one of its semiempirical extensions, for the activity coefficient. These formulas, which relate $\log f_i$ to the ionic strength, $\mu$,[6] become more accurate representations of $f_i$ as the solution becomes more dilute. Most important, however, is the fact that the plot of $pK_2'$ [7] with respect to ionic strength is often nearly linear over much of the experimental range, and an extrapolation to zero ionic strength, yielding the true value of $pK_2$, is made without difficulty. The value of $pK_2$ is independent of any assumptions regarding the validity of the expressions for $f_i$ that were chosen as an aid to extrapolation [1].

Substitution of the Debye-Hückel limiting-law expression for each activity coefficient in eq 9 gives for $pK_2'$

$$pK_2' = (E-E°)/k + \log(m_{H_2PO_4} m_{Cl}/m_{HPO_4}) + 2A\sqrt{\mu}, \tag{10}$$

where $A$ is a constant for aqueous solutions at a particular temperature. Values of $pK_2'$ from eq 10 approach the true value of $pK_2$ in dilute solutions.

An approximation much closer to the experimental activity coefficients than is given by the limiting law may be obtained from the

[6] The ionic strength is defined by $\mu = \Sigma m_i z_i^2/2$, where $z_i$ is the valence of an ion species of molality $m_i$. For the solutions used here, where $m_1 = m_3$, $\mu = 2m_1 + 3m_2$.

[7] $pK_2'$ is the negative logarithm of the "apparent" dissociation constant obtained in eq 9 by use of any approximate values for $f_i$ (*cf.* eq 10).

equation of Guggenheim [22] or from the Debye-Hückel formula, based theoretically on recognition of a finite mean lower limit for the distance of approach of the ions, represented by the parameter $a_i$; Hückel [23] extended the usefulness of the latter equation still higher in the range of ionic strengths by adding a term linear in $\mu$. The change of the activity coefficient of any ion species $i$ as a function of ionic strength is thus best represented in terms of two general constants, $A$ and $B$, and two adjustable parameters, $a_i$ and $\beta$, in the equation

$$-\log f_i=\frac{A z_i^2\sqrt{\mu}}{1+Ba_i\sqrt{\mu}}-\beta\mu. \tag{11}$$

The values of $a_i$ and $\beta$ are averages characteristic of the mixture, depending upon the specific properties of the ions that compose the mixture and upon the relative ionic concentrations. The constants $A$ and $B$ vary only with the dielectric constant and temperature.[8]

When each activity coefficient of eq 9 is expressed in the form of eq 11, the dissociation constant becomes

$$\mathrm{p}K_2=[(E-E^\circ)/k+\log(m_{\mathrm{H_2PO_4}}m_{\mathrm{Cl}}/m_{\mathrm{HPO_4}})+2A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})]+\beta\mu. \tag{12}$$

All quantities on the right side of eq 12 are known, with the exception of the parameters $a_i$ and $\beta$. Further, provided eq 11 is adequate to express the change of activity coefficient with ionic strength, it is evident that there will be a particular value of $a_i$ for which $\mathrm{p}K_2'$, the expression in brackets (eq 12), will be a linear function of $\mu$, that is,

$$\mathrm{p}K_2=\mathrm{p}K_2'+\beta\mu. \tag{13}$$

Computations of $\mathrm{p}K_2'$ were therefore made at each temperature for several values of $a_i$ until the most satisfactory straight line was established. The slope of this plot of $\mathrm{p}K_2'$ with respect to $\mu$ gives the value of the parameter $\beta$; the intercept at zero ionic strength is $\mathrm{p}K_2$, the negative common logarithm of the true, or "thermodynamic," dissociation constant.

### 3. pH VALUES OF THE PHOSPHATE-CHLORIDE MIXTURES

It is implied in the foregoing discussion that the activity coefficient of chloride ion, $f_{\mathrm{Cl}}$, in each of the solutions studied can be computed from eq 11 with the use of the numerical values of the average parameters $a_i$ and $\beta$ for the 13 temperatures. Hence, combination of eq 7 and 11 gives an expression which makes possible the calculation of the pH values at any temperature directly from the emf and the composition of the solution:

$$\mathrm{pH}=(E-E^\circ)/k+\log m_{\mathrm{Cl}}-A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+\beta\mu. \tag{14}$$

## III. ERRORS OF METHOD AND SIMPLIFICATIONS

### 1. BUFFER RATIO

The successful application of eq 12 to a determination of $\mathrm{p}K_2$ requires an accurate knowledge of the ratio of primary phosphate ion to secondary phosphate ion. This quantity, $m_{\mathrm{H_2PO_4}}/m_{\mathrm{HPO_4}}$, is the

[8] The dielectric constant is assumed to be constant with changing ionic strength and to be the same as the gross dielectric constant of pure water.

"buffer ratio", and its value is derived from the known molalities of the primary and secondary alkali metal phosphates of which the cell solutions are composed. As a result of dissociation and hydrolysis, however, the true ratio of the ions is not always the same as the ratio of the stoichiometrical molalities of the buffer salts.

From the equilibrium constants for eq 1 and 3 [9] it may be shown that the quantity of $H_3PO_4$ is less than 0.01 percent of the $H_2PO_4^-$ in solutions whose pH values lie between 6 and 8, whereas the amount of $PO_4^{\equiv}$ is less than 0.05 percent of the total $HPO_4^=$. The maximum error of 0.05 percent in the buffer ratio caused by neglect of the phosphoric acid and trivalent phosphate ion corresponds to about 0.0002 pH unit, or somewhat less than 0.02 mv in the emf. This error is slightly less than the experimental uncertainty inherent in the measurement.

The possibility of the formation of $HPO_4^=$ by the dissociation of $H_2PO_4^-$, or of the combination of $HPO_4^=$ with hydrogen ion to form $H_2PO_4^-$, upon solution of the phosphate salts in water demands particular attention, for such changes in composition alter the numerator and denominator of the buffer ratio in opposite directions.

Since the influence of the first and third dissociation equilibria (eq 1 and 3) has been shown to be negligible, any deviation of the pH of the mixture from that of pure water may be ascribed to eq 2 and 4. For the most dilute solution of the smallest buffer ratio (solution C9), these reactions cause a maximum change in buffer ratio which corresponds to 0.0005 in pH and $pK_2$, or about 0.03 mv in the emf. The stoichiometrical ratio, then, may be used as the buffer ratio in solutions having pH values between 6 and 8 without dissociation or hydrolysis corrections.

## 2. EFFECT OF CARBONATE

The titration of the first acid group of carbonic acid is complete at a pH value near 8.5, in a 0.1 *M* solution. Any carbonate impurity in these phosphate buffer solutions would be present, then, chiefly as dissolved carbon dioxide (or carbonic acid) and bicarbonate ion and would be removed only slowly by the bubbling hydrogen. Likewise, the reaction of carbon dioxide with the disodium salt during recrystallization would yield bicarbonate. The technique to be described later for making weight dilutions with carbon-dioxide-free water in an inert atmosphere precludes the possibility of contamination of the solutions at the time of their preparation.

A calculation of the effect of carbonate impurity on the pH value of a buffer solution may be performed readily with the use of approximate values for the dissociation constants of phosphoric acid, carbonic acid, and water.

Carbonate ion, as well as phosphoric acid and trivalent phosphate ion, is present in negligible quantity at pH values between 6 and 8. For a mixture of sodium bicarbonate, sodium dihydrogen phosphate, and disodium hydrogen phosphate, in which the total molality of phosphate in all forms is designated by $X$ and the total carbonate by $Y$, the hydrogen-ion activity may be expressed in terms of $X$; $Y$; the second dissociation constant of phosphoric acid, $K_2$; the first dissociation constant of carbonic acid, $K_4$ [25, 26]; the ionization constant

[9] $pK_1$ (25°)=2.124 (Nims [24]); $pK_3$ (25°)=12.325 (Bjerrum and Unmack [4]).

of water, $K_w$ [27]; the sodium-ion molality; and activity coefficients, as follows:

$$\frac{YK_4}{K_4+a_H f_{HCO_3}}=\frac{a_H}{f_H}-\frac{K_w}{a_H f_{OH}}+m_{Na}-X\left[\frac{2K_2 f_{H_2PO_4}+a_H f_{HPO_4}}{K_2 f_{H_2PO_4}+a_H f_{HPO_4}}\right]. \quad (15)$$

Consider a solution 0.05 $m$ with respect to sodium dihydrogen phosphate and to disodium hydrogen phosphate. When appropriate values for the activity coefficients (calculated from eq 11 with $a_i=4.0$ and $\beta=0.0993$) are substituted in eq 15, the pH of this solution in the absence of carbonate is found to be 6.775. For a solution in which each of the phosphate salts is present at a molality of 0.005, the pH will be 7.024.

Absorption of carbon dioxide by the first solution in amount corresponding to 0.1 mole percent of the total phosphate, $X$, would yield a mixture having the composition: 0.0501 $m$ sodium dihydrogen phosphate, 0.0499 $m$ disodium hydrogen phosphate, and 0.0001 $m$ sodium bicarbonate. The pH value computed for this mixture is 6.773. The same relative amount of carbonate in the 0.005 $m$ solution changes the value of that solution to 7.022. The lowering of pH which attends the absorption of 0.1 mole percent carbonate is 0.002 pH unit in each case. As the salts used contained no detectable carbonate and utmost precautions were used to exclude atmospheric carbon dioxide during the preparation of the solutions, it is believed that errors from the possible presence of carbonates are less than 0.001 pH.

## IV. EXPERIMENTAL METHODS

The design of the equipment and the experimental procedure differed principally from those described by Hamer and Acree [28] in the following respects. The cells were mounted individually and connected to the hydrogen-supply manifold by standard joints. It was thus possible to clean, dry, and fill the cells outside the bath. The use of solutions having pH values of 7 or above necessitated special precautions in the exclusion of carbon dioxide, and led to a technique for making weight dilutions while keeping the solutions in an atmosphere of purified nitrogen.

### 1. EQUIPMENT

Figure 2 is a side view of a brass rack holding 5 of the cells, and figure 3 shows the 55-gallon water thermostat with the 10 cells in position and connected to the hydrogen-supply manifold.

The thermostat was equipped with 2 heating units which provided 12 stages of intermittent or constant heat ranging in power consumption from 200 to 4,000 watts. At the highest rate of heating, 20 to 30 minutes was ordinarily required to raise the water temperature 5 degrees. A refrigerator compressor unit served to lower the temperature. It was also used in conjunction with the heaters to control the temperature between 0° and 25° C.

The thermoregulator contained about 160 ml of mercury. A small reservoir for excess mercury, separated by a stopcock from one arm of the regulator, permitted control of the temperature at any point between 0° and 60° C without undue change in the height of the mercury in the capillary tube which carried the platinum-wire contact.

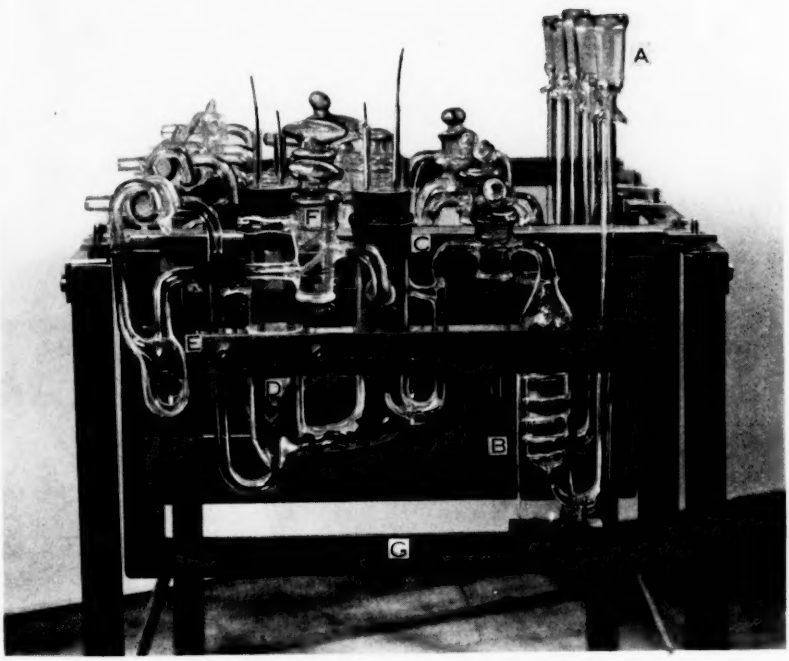


FIGURE 2.—*Side view of one of the cells.*

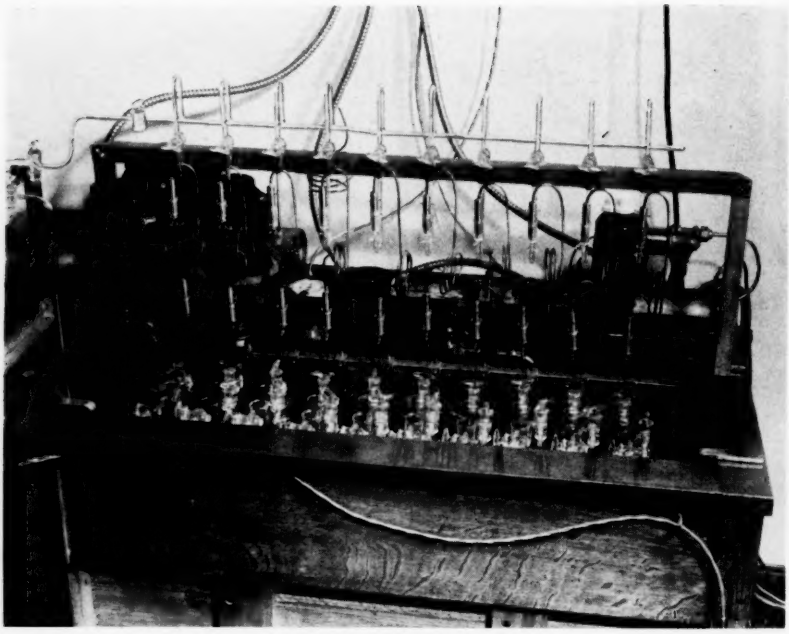

FIGURE 3.—*Thermostat with 10 cells in place.*

Each cell is connected with the hydrogen supply manifold by copper tubing carrying brass standard-taper joints.

The details of the cell are shown in figure 2. The cells were constructed of Pyrex glass and were supported individually on brass frames, shown at *G*. In operation, hydrogen enters at the standard-taper joint, *A*, having passed from the hydrogen manifold above the bath through the copper capillary tubing which leads to the cell. The copper was soldered at either end to tapered brass joints ground to fit the standard glass joints of the cells and manifold. In the equilibrator, *B*, the gas bubbles slowly through cell solution. This arrangement precludes the possibility of dilution or concentration of the solution in the hydrogen electrode compartment, *C*, through which the gas passes next. In the operation of the cell, compartment *D* houses two silver–silver-chloride electrodes.

Hydrogen escapes from the cell through the three-way stopcock, *F*, and the detachable trap, *E*, provided with a vertical exit tube which extends above the level of the water in the bath and is bent through 180° at the upper end to retard the entrance of air. The tube which conducts hydrogen from the cell into the trap terminates about 2 cm from the bottom of the trap. This construction ensured that the small quantity of solution that might be forced out of the hydrogen-electrode compartment by the flow of hydrogen would not block the bottom of the gas tube and cause an increase in the pressure of the gas within the system.

When the cells were immersed to the top of compartments *C* and *D* (fig. 2) the emf readings were identical with those obtained when they were completely immersed. Equilibrium conditions of temperature and vapor pressure were probably established in all cases.

Except at 0°, it was found convenient to adjust the bath within ±0.02° of the desired temperature. For the cells of highest temperature coefficient, this range of temperature corresponds to slightly over 0.02 mv in emf, or about 0.0004 pH unit. The thermometer was graduated in tenths of a degree, and 0.01° could be estimated with the aid of a lens. It was checked by comparison with a thermometer calibrated by the Thermometry Section of this Bureau. Zero-point corrections were made from time to time.

The electromotive forces were measured with a Leeds & Northrup type K potentiometer. A cell which contained potassium dihydrogen phosphate, disodium hydrogen phosphate, and sodium chloride, each at a molality of approximately 0.01, was found to have a resistance of 750 ohms at 25° C. A Leeds & Northrup type R galvanometer with critical damping was employed in conjunction with the potentiometer as a null-point instrument. The galvanometer coil had a resistance of 550 ohms. The standard cell was a saturated cell of low temperature coefficient [29]. The potentiometer and standard cell were calibrated by the Resistance Measurements Section and the Electrochemistry Section, respectively, of this Bureau.

## 2. MATERIALS

Disodium hydrogen phosphate, potassium dihydrogen phosphate, and sodium chloride were obtained as reagent-grade salts which conformed with American Chemical Society specifications. In addition, qualitative tests on the phosphates showed aluminum to be absent. Disodium hydrogen phosphate dodecahydrate was found

to fuse when dehydration at 80° to 100° C was attempted. The salt, purified by three recrystallizations from redistilled water, was therefore dried in air at room temperature for 3 days. Drying the preparation in the oven at 110° to 130° C was then possible. Ignition of the anhydrous salt to pyrophosphate in a platinum crucible indicated the presence of from 0.02 to 0.04 percent of volatile impurity (assumed to be water). Quantitative tests for carbonate by evolution and absorption of carbon dioxide using 10-g samples of the phosphate, showed the absence of weighable amounts of this impurity. Weight titrations of three samples of the anhydrous disodium hydrogen phosphate with hydrochloric acid solution with the use of naphthyl red indicator gave 100.06, 100.04, and 100.06 percent, respectively, for the degree of neutralization of the second acid hydrogen. A standard comparison solution prepared from indicator, water, and the appropriate amount of potassium dihydrogen phosphate was used to facilitate the recognition of the endpoint.

Five analyses of the disodium hydrogen phosphate by weighing magnesium pyrophosphate were performed by the Reagents and Platinum Metals Section of this Bureau. The results gave 99.995 percent of $Na_2HPO_4$, with an average deviation of 0.030 percent.

The potassium dihydrogen phosphate was recrystallized three times; the first and last recrystallizations were made from redistilled water and the second from alcohol, which removes potassium bromide. Oven-drying at 130° C readily removed the last traces of water, as evidenced by the loss of weight on ignition of samples of the salt to form the metaphosphate. Four analyses of the potassium dihydrogen phosphate, which were made by the Reagents and Platinum Metals Section, gave 100.003 percent of $KH_2PO_4$, with an average deviation of 0.008 percent.

The sodium chloride was recrystallized twice from redistilled water.

Hydrochloric acid of reagent grade was diluted to a concentration near that of the azeotropic mixture and was distilled in an all-glass still. The middle third of the distillate was retained for use. About 18 liters of approximately 0.1 *M* acid was prepared by dilution of this fraction and was used in the preparation of the solutions for the determination of the second dissociation constant. This stock solution was standardized gravimetrically by the precipitation and weighing of silver chloride.

A correction for the solubility of silver chloride in the wash solution was applied. The mean deviation from the mean value of six analyses was 0.04 percent.

Nitrogen used in de-aerating the cell solutions was purified by a modification of the method of Van Brunt [30]. It was passed through two scrubbers containing a mixture of equal parts of ammonium hydroxide and saturated ammonium carbonate in contact with copper strips, then through two bottles of 1 *M* sulfuric acid, a tower of soda lime, and finally through a wash bottle of distilled water. Ammonia was shown to be absent from the nitrogen by passing a slow stream of the gas through a mixture of dilute hydrochloric acid, a few drops of methyl orange solution, and enough dilute alkali to cause partial conversion of the indicator. The color remained unaltered by prolonged bubbling of the gas.

Tank hydrogen was used in the cells. Traces of carbon dioxide and oxygen were removed as described by Hamer and Acree [28], except

that the gas which left the palladinized asbestos unit was further treated by contact with reduced copper oxide heated to about 450° C. It was then conducted through copper tubing of small diameter to the hydrogen-supply manifold above the bath.

The water used in making the cell solutions was distilled from alkaline permanganate and redistilled in a current of carbon-dioxide-free air. The conductance of the water was approximately $0.8\times10^{-6}$ mho.

### 3. SOLUTIONS

Figure 4 shows schematically the apparatus assembly employed in the transfer of portions of the stock solution to each of the 10 solution flasks out of contact with air.

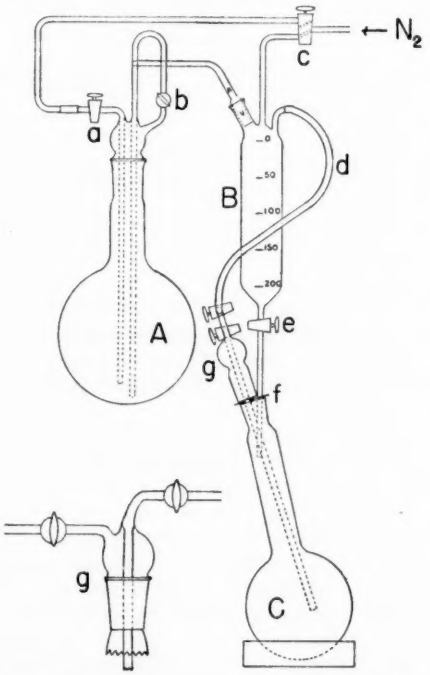


FIGURE 4.—*Schematic diagram of apparatus employed in transferring portions of the stock solution to solution flasks without the danger of contamination by carbon dioxide.*

The stock solution for each series of cells was prepared in the stock-solution flask, *A*, from weighed portions of powdered disodium hydrogen phosphate and of hydrochloric acid solution or, in the case of series B*, from weighed portions of sodium chloride, potassium dihydrogen phosphate, disodium hydrogen phosphate, and water. With stopcock *b* closed, nitrogen forced the stock solution into the 200-ml buret, *B*, which had been flushed previously with nitrogen. With the buret filled, stopcock *c* was rotated 180°, and the gas was passed through the rubber tube, *d*, to the solution flask, *C*, of 1-liter capacity, in which the dilution was made. The structure of the top

of a solution flask is shown at *g*. With the nitrogen flowing, the desired amount of stock solution was drawn through stopcock *e* into the flask, *C*. The flask was then weighed and the proper quantity of water added with the inert gas flowing through *C*. After the dilutions were completed, nitrogen was passed at the rate of about 2 bubbles per second through all 10 solution flasks for 1 to 2 hours before the final weighings were made. Vacuum corrections were made on all weighings.

## 4. ELECTRODES

Hydrogen and silver–silver-chloride electrodes were always used in pairs, two electrodes of the same kind being mounted in the same rubber stopper. In this way, it was possible to check the agreement of each pair of electrodes after the cell had been made up and to detect any changes or side reactions which affected the two electrodes unequally.

The platinum foils that formed the bases for the hydrogen electrodes were 8 mm wide and 15 mm long. They were coated lightly with spongy platinum by electrolysis in 3-percent chloroplatinic acid solution for 1 minute at a current of 300 ma. Ten milligrams of lead acetate was added to each 100 ml of chloroplatinic acid solution. A reversing switch on the current supply permitted either foil to be used as anode during the deposition of platinum black on the other. The electrodes were ordinarily freshly plated for each run and were soaked in distilled water before use.

The silver–silver-chloride electrodes were of the thermal-electrolytic type. They were prepared by the method described in an earlier publication from this Bureau [28]. These electrodes also were usually remade for each series of experiments. After preparation, they were soaked in distilled water for several hours.

For the purpose of intercomparing hydrogen or silver–silver-chloride electrodes in 0.05 *M* hydrochloric acid before their use in pH measurements, vessels with six necks were constructed from 1-liter round-bottomed flasks. These vessels accommodated six pairs of electrodes and hydrogen supply and exit tubes. Measurable differences (larger than 0.01 mv) among the hydrogen electrodes were rarely found, although silver–silver-chloride electrodes occasionally differed by 0.05 mv. Pairs of electrodes that showed differences of as much as 0.1 mv were rejected.

The evacuation method was used in filling most of the cells. Later, the danger of concentration polarization at the silver electrode was obviated by soaking each pair of electrodes overnight in a portion of the particular solution in which they were to be used.

## 5. PROCEDURE

With the cell in position for filling, the flask containing the solution was attached at *A* (fig. 2) by a standard joint of glass. The hydrogen supply was connected to the solution flask and to the three-way stopcock, *F*, of the cell in such fashion that the gas could be used to force solution from the flask through *A* into the cell or could be led in through *F*, to expel solution through the tube attached to the base of *D*. The trap, *E*, was removed during the filling of the cell, and a thick-

walled rubber tube leading to an oil pump was attached to the cell in its place.

When the electrodes had not been soaked previously in the buffer solution but had been stored in distilled water, they were dried superficially, fixed in place, and the entire cell evacuated for 5 to 10 minutes. The stopcock of the solution flask was then opened and the cell filled with solution. This wash solution was expelled by hydrogen pressure and the cell refilled. When the silver–silver-chloride electrodes had been soaked in buffer solution, the cell was not evacuated but was flushed with hydrogen before the wash solution was admitted.

The initial emf measurements were made at 25° C. Two hours was ordinarily sufficient to attain equilibrium. After constant emf values had been maintained for at least 2 hours, the temperature of the bath was lowered to 0.2° to 0.5° C, the lowest temperature at which measurements were made; a short, unambiguous extrapolation with the aid of the temperature coefficient yielded the emf at 0° C. The bath was raised at 5-degree intervals to 60° C and was finally brought back to 25° C. Three sets of emf measurements at 25° C were thus obtained. The measurements usually required about 2 hours at each temperature. The entire series of experiments was ordinarily completed in 3 days. Cells whose final readings at 25° C differed from the initial equilibrium values by more than 0.18 mv (corresponding to 0.003 pH unit) were rejected as unsatisfactory.

## V. CALCULATION OF THE DISSOCIATION CONSTANT

The electromotive forces recorded in five satisfactory series of experiments at three different buffer ratios were corrected to a pressure of 760 mm of hydrogen (unit activity) in the usual way [31]. The corrected values for the 13 temperatures are listed in tables 1, 2, and 3. Series A solutions contained $H_2PO_4^-$ and $HPO_4^=$ in the ratio 1.0132. The buffer ratios for series B and C solutions were 1.5684 and 0.6540, respectively. Series B* differed from series B in that potassium dihydrogen phosphate was used in place of sodium dihydrogen phosphate. The buffer ratio was the same in both series.

When $pK_2'$, the expression in square brackets in eq 12, was computed for various values of $a_i$, the average ion-size parameter, it was found that a value of approximately 4 A would give the desired linear change of $pK_2'$ with ionic strength. It was evident, however, that a slope of zero would not be obtained.

The adjustment of $a_i$ was made to the nearest 0.1 A to yield the best extrapolation at each temperature. Within the error of the experiments, the same value of $a_i$ was found to apply to the three buffer ratios at any particular temperature. There was a small variation of $a_i$ with temperature. The slope of the plot of $pK_2'$ with respect to $\mu$ is numerically equal to $\beta$, as may be seen from eq 13. The values of $k$, $a_i$, $3A$, $Ba_i$, and $\beta$ for each temperature and series of solutions are given in table 4.[10]

[10] Numerical values of $A$, $B$, and $k$ at 5-degree intervals from 0° to 60° C have been recalculated by Harned, Burton, and Acree [16, table 2] from reliable values of the faraday, the electronic charge, the Boltzmann constant, and the dielectric constant. Their values of $k$ are given in absolute volts. Conversion to International volts has been made by dividing by 1.00034 [20].

TABLE 1.—*Electromotive forces of hydrogen–silver-chloride cells containing phosphate-chloride mixtures*

SERIES A

| Solution number | $m_1=m_3$ | $m_2$ | $E_0°$ | $E_5°$ | $E_{10}°$ | $E_{15}°$ | $E_{20}°$ |
|---|---|---|---|---|---|---|---|
| A1 | 0.09079 | 0.08961 | 0.66626 | 0.67011 | 0.67382 | 0.67754 | 0.68131 |
| A2 | .07340 | .07245 | .67289 | .67680 | .68059 | .68436 | .68823 |
| A3 | .05507 | .05435 | .68185 | .68593 | .68987 | .69379 | .69780 |
| A4 | .03726 | .03678 | .69361 | .69761 | .70190 | .70612 | .71009 |
| A5 | .03017 | .02977 | .69960 | .70399 | .70822 | .71244 | .71676 |
| A6 | .010491 | .010354 | .72970 | .73447 | .73923 | .74398 | .74884 |
| A7 | .09079 | .08915 | .66635 | .67007 | .67380 | .67751 | .68133 |
| A8 | .07475 | .07340 | .67240 | .67624 | .68005 | .68381 | .68775 |
| A9 | .05199 | .05105 | .68328 | .68758 | .69156 | .69552 | .69954 |
| A10 | .03592 | .03527 | .69457 | .69871 | .70289 | .70705 | .71133 |
| A11 | .018456 | .018122 | .71387 | .71832 | .72279 | .72725 | .73185 |
| A12 | .015090 | .014818 | .71954 | .72411 | .72871 | .73326 | .73795 |
| A13 | .010151 | .009968 | .73058 | .73536 | .74013 | .74489 | .74982 |
| A14 | .008598 | .008442 | .73518 | .73996 | .74482 | .74967 | .75472 |
| A15 | .005978 | .005870 | .74507 | .75000 | .75503 | .76004 | .76525 |
| A16 | .004213 | .004137 | .75434 | .75952 | .76467 | .76984 | .77525 |

| Solution number | $E_{25}°$ | $E_{30}°$ | $E_{35}°$ | $E_{40}°$ | $E_{45}°$ | $E_{50}°$ | $E_{55}°$ | $E_{60}°$ |
|---|---|---|---|---|---|---|---|---|
| A1 | 0.68515 | 0.68900 | 0.69281 | 0.69672 | 0.70058 | 0.70445 | 0.70834 | 0.71222 |
| A2 | .69228 | .69616 | .70012 | .70399 | .70793 | .71198 | .71595 | .71999 |
| A3 | .70191 | .70606 | .71016 | .71420 | .71836 | .72243 | .72657 | .73075 |
| A4 | .71455 | .71872 | .72303 | .72738 | .73166 | .73596 | .74030 | .74468 |
| A5 | .72119 | .72564 | .73014 | .73451 | .73900 | .74355 | .74808 | .75263 |
| A6 | .75382 | .75879 | .76383 | .76882 | .77380 | .77880 | .78385 | .78893 |
| A7 | .68510 | .68904 | .69281 | .69670 | .70049 | .70443 | .70830 | .71211 |
| A8 | .69160 | .69562 | .69933 | .70343 | .70737 | .71124 | .71521 | .71920 |
| A9 | .70370 | .70813 | .71219 | .71640 | .72045 | .72457 | .72885 | .73306 |
| A10 | .71560 | .72008 | .72443 | .72880 | .73308 | .73746 | .74175 | .74610 |
| A11 | .73653 | .74138 | .74604 | .75082 | .75551 | .76028 | .76494 | .76975 |
| A12 | .74268 | .74752 | .75228 | .75713 | .76189 | .76670 | .77154 | .77641 |
| A13 | .75471 | .75980 | .76475 | .76981 | .77483 | .77993 | .78494 | .79014 |
| A14 | .75972 | .76495 | .77095 | .77518 | .78028 | .78539 | .79052 | .79573 |
| A15 | .77045 | .77592 | .78118 | .78652 | .79178 | .79714 | .80240 | .80782 |
| A16 | .78059 | .78626 | .79168 | .79716 | .80265 | .80817 | .81354 | .81912 |

TABLE 2.—*Electromotive forces of hydrogen–silver-chloride cells containing phosphate-chloride mixtures*

SERIES B

| Solution number | $m_1=m_3$ | $m_2$ | $E_0°$ | $E_5°$ | $E_{10}°$ | $E_{15}°$ | $E_{20}°$ |
|---|---|---|---|---|---|---|---|
| B1 | 0.09079 | 0.05789 | 0.65677 | 0.66023 | 0.66365 | 0.66701 | 0.67077 |
| B2 | .07410 | .04725 | .66341 | .66712 | .67076 | .67440 | .67809 |
| B3 | .05294 | .03375 | .67355 | .67740 | .68123 | .68499 | .68884 |
| B4 | .03459 | .02205 | .68629 | .69027 | .69431 | .69826 | .70237 |
| B5 | .02343 | .014937 | .69757 | .70190 | .70608 | .71028 | .71456 |
| B6 | .014911 | .009507 | .71039 | .71480 | .71923 | .72362 | .72812 |
| B7 | .009764 | .006226 | .72237 | .72696 | .73159 | .73625 | .74101 |
| B8 | .007546 | .004811 | .72924 | .73388 | .73857 | .74328 | .74812 |
| B9 | .005365 | .003420 | .73851 | .74335 | .74825 | .75319 | .75819 |

SERIES B*

| Solution number | $m_1=m_3$ | $m_2$ | $E_0°$ | $E_5°$ | $E_{10}°$ | $E_{15}°$ | $E_{20}°$ |
|---|---|---|---|---|---|---|---|
| B*1 | 0.09077 | 0.05787 | 0.65774 | 0.66132 | 0.66493 | 0.66850 | 0.67211 |
| B*2 | .05151 | .03284 | .67499 | .67884 | .68271 | .68652 | .69040 |
| B*3 | .01604 | .02935 | .67831 | .68226 | .68622 | .69002 | .69394 |
| B*4 | .02877 | .018341 | .69206 | .69619 | .70032 | .70434 | .70850 |
| B*5 | .009373 | .005976 | .72335 | .72806 | .73277 | .73739 | .74216 |
| B*6 | .006059 | .003863 | .73499 | .73990 | .74481 | .74969 | .75468 |
| B*7 | .004099 | .002614 | .74543 | .75056 | .75565 | .76071 | .76590 |
| B*8 | .002835 | .0018073 | .75509 | .76034 | .76561 | .77080 | .77612 |

TABLE 2.—*Electromotive forces of hydrogen–silver-chloride cells containing phosphate-chloride mixtures*—Continued

SERIES B—Continued

| Solution number | $E_{25}°$ | $E_{30}°$ | $E_{35}°$ | $E_{40}°$ | $E_{45}°$ | $E_{50}°$ | $E_{55}°$ | $E_{60}°$ |
|---|---|---|---|---|---|---|---|---|
| B1 | 0.67466 | 0.67840 | 0.68217 | 0.68583 | 0.68947 | 0.69309 | 0.69684 | 0.70052 |
| B2 | .68183 | .68560 | .68948 | .69278 | .69665 | .70053 | .70456 | .70823 |
| B3 | .69276 | .69662 | .70069 | .70470 | .70863 | .71261 | .71656 | .72041 |
| B4 | .70659 | .71068 | .71494 | .71915 | .72328 | .72750 | .73170 | .73592 |
| B5 | .71897 | .72334 | .72799 | .73241 | .73674 | .74133 | .74580 | .75027 |
| B6 | .73276 | .73730 | .74182 | .74650 | .75111 | .75584 | .76053 | .76520 |
| B7 | .74583 | | | | | | | |
| B8 | .75316 | | | | | | | |
| B9 | .76338 | .76843 | .77369 | .77893 | .78415 | .78935 | .79470 | .79984 |

SERIES B*—Continued

| Solution number | $E_{25}°$ | $E_{30}°$ | $E_{35}°$ | $E_{40}°$ | $E_{45}°$ | $E_{50}°$ | $E_{55}°$ | $E_{60}°$ |
|---|---|---|---|---|---|---|---|---|
| B*1 | 0.67567 | 0.67938 | 0.68317 | 0.68684 | 0.69053 | 0.69419 | 0.69790 | 0.70166 |
| B*2 | .69430 | .69825 | .70235 | .70646 | .71045 | .71445 | .71850 | .72257 |
| B*3 | .69787 | .70191 | .70607 | .70992 | .71413 | .71825 | .72227 | .72638 |
| B*4 | .71271 | .71709 | .72149 | .72579 | .73012 | .73441 | .73875 | .74315 |
| B*5 | .74694 | .75183 | .75684 | .76177 | .76671 | .77168 | .77667 | .78175 |
| B*6 | .75965 | .76482 | .77010 | .77530 | .78051 | .78574 | .79101 | .79633 |
| B*7 | .77097 | .77643 | | | | | | |
| B*8 | .78151 | .78698 | .79257 | .79806 | .80353 | .80912 | .81467 | .82030 |

TABLE 3.—*Electromotive forces of hydrogen–silver-chloride cells containing phosphate-chloride mixtures*

SERIES C

| Solution number | $m_1 = m_3$ | $m_2$ | $E_0°$ | $E_5°$ | $E_{10}°$ | $E_{15}°$ | $E_{20}°$ |
|---|---|---|---|---|---|---|---|
| C1 | 0.09079 | 0.13882 | 0.67584 | 0.67976 | 0.68365 | 0.68755 | 0.69145 |
| C2 | .06661 | .10185 | .68536 | .68943 | .69346 | .69750 | .70157 |
| C3 | .04820 | .07371 | .69514 | .69936 | .70356 | .70776 | .71195 |
| C4 | .02578 | .03943 | .71353 | .71803 | .72250 | .72701 | .73156 |
| C5 | .011957 | .018283 | .73534 | .74018 | .74506 | .74996 | .75490 |
| C6 | .007914 | .012102 | .74679 | .75183 | .75691 | .76198 | .76715 |
| C7 | .004944 | .007560 | | .76467 | .77006 | .77545 | .78087 |
| C8 | .002943 | .004501 | .77347 | .77900 | .78455 | .79015 | .79577 |
| C9 | .0019314 | .002953 | .78435 | .79009 | .79587 | .80167 | .80758 |

SERIES C—Continued

| Solution number | $E_{25}°$ | $E_{30}°$ | $E_{35}°$ | $E_{40}°$ | $E_{45}°$ | $E_{50}°$ | $E_{55}°$ | $E_{60}°$ |
|---|---|---|---|---|---|---|---|---|
| C1 | 0.69533 | 0.69950 | 0.70322 | 0.70744 | 0.71148 | 0.71520 | 0.71932 | 0.72339 |
| C2 | .70575 | .71001 | .71404 | .71818 | .72248 | .72651 | .73080 | .73502 |
| C3 | .71622 | .72065 | .72474 | .72909 | .73358 | .73774 | .74220 | .74675 |
| C4 | .73612 | .74098 | .74550 | .75017 | .75507 | .75979 | .76455 | .76935 |
| C5 | .75993 | .76513 | .77017 | .77530 | .78042 | .78556 | .79080 | .79619 |
| C6 | .77240 | | | | | | | |
| C7 | .78622 | .79205 | .79767 | | | | | |
| C8 | .80152 | .80755 | .81329 | .81914 | .82501 | .83089 | .83682 | .84277 |
| C9 | .81338 | .81973 | .82573 | .83184 | .83793 | .84403 | .85007 | .85613 |

TABLE 4.—*Numerical values of k, 3A, $a_i$, $Ba_i$, and β at temperatures from 0° to 60° C for series A, B, B*, and C solutions*

| t | k | 3A | $a_i$ | $Ba_i$ | β (series A) | β (series B) | β (series B*) | β (series C) |
|---|---|---|---|---|---|---|---|---|
| °C | *Int. v* | | *A* | | | | | |
| 0 | 0.05418 | 1.4670 | 3.5 | 1.1386 | 0.098 | 0.160 | 0.103 | 0.046 |
| 5 | .05517 | 1.4784 | 3.6 | 1.1740 | .091 | .153 | .104 | .043 |
| 10 | .05616 | 1.4901 | 3.7 | 1.2099 | .095 | .157 | .101 | .046 |
| 15 | .05715 | 1.5027 | 3.8 | 1.2460 | .091 | .158 | .097 | .046 |
| 20 | .05814 | 1.5159 | 3.8 | 1.2498 | .087 | .149 | .096 | .044 |
| 25 | .05914 | 1.5294 | 3.8 | 1.2532 | .081 | .140 | .093 | .040 |
| 30 | .06013 | 1.5441 | 3.8 | 1.2574 | .077 | .137 | .093 | .036 |
| 35 | .06112 | 1.5591 | 3.8 | 1.2616 | .081 | .136 | .081 | .043 |
| 40 | .06211 | 1.5750 | 3.8 | 1.2654 | .073 | .131 | .079 | .037 |
| 45 | .06311 | 1.5909 | 4.0 | 1.3368 | .093 | .152 | .098 | .050 |
| 50 | .06410 | 1.6074 | 4.0 | 1.3412 | .087 | .150 | .095 | .056 |
| 55 | .06509 | 1.6251 | 4.0 | 1.3464 | .081 | .137 | .091 | .049 |
| 60 | .06608 | 1.6434 | 4.0 | 1.3512 | .084 | .144 | .094 | .051 |

The effect of various $a_i$ values on the course of the extrapolation is evident in figure 5, where $pK'_2$ from the measurements of solutions A7 to A16 is plotted as a function of ionic strength. Curve *A* was computed with the use of the Debye-Hückel limiting-law expression for the activity coefficients of the phosphate and chloride ions (eq 10). The four lower curves were derived from eq 12; $pK'_2$ represents the quantity in brackets.[11] An $a_i$ parameter of 3.04 A was used for curve *B*, 3.5 A for curve *C*, 4.0 A for curve *D*, and 4.5 A for curve *E*. Careful examination shows that curves *A*, *B*, and *C* are concave downward, *D* is very nearly straight, and *E* is concave upward. Actually,

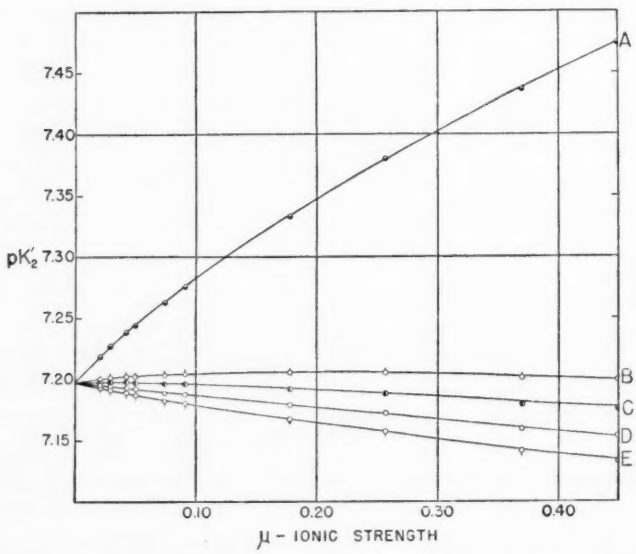


FIGURE 5.—*Extrapolation plots for the second dissociation constant.*

Curve *A* was computed from eq 10; curves *B*, *C*, *D*, and *E* were obtained with the use of eq 12 with $a_i$ values of 3.04, 3.5, 4.0, and 4.5, respectively.

[11] Curve *A* likewise may be considered to be calculated from eq 12 with $a_i$=0, as is easily seen from comparison of eq 10 and 12.

$pK_2'$ is most nearly a linear function of $\mu$ when an $a_i$ value of 3.8 A is employed.

With the use of the $\beta$ values for each series of solutions at the 13 temperatures, values of $pK_2$ were computed from eq 13 for each solution measured. Figure 6 is a graph of all values of $pK_2$ for the three buffer ratios at 0°, 25°, and 60° C. The average value of

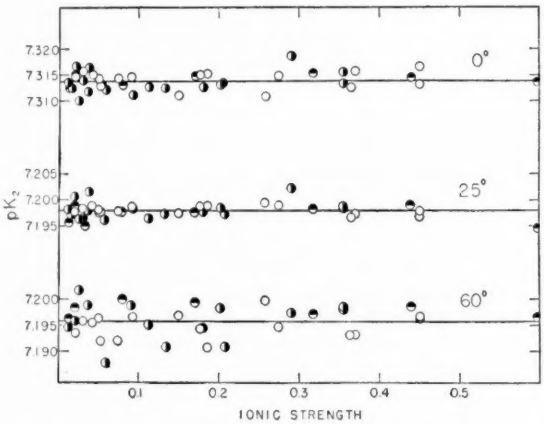


FIGURE 6.—*Plots of all values of* $pK_2$ *(eq 12) at 0°, 25°, and 60° C as a function of ionic strength.*

○ = series A; ◑ = series B and B*; ◓ = series C

$pK_2$ for each series is given in table 5. The mean value for the five series, weighting each one equally, is given in the next to the last column of the table, together with the mean departure from the mean. The largest uncertainty is inherent in the value at 60° and corresponds to 0.12 mv, or 0.002 in $pK_2$..

TABLE 5.—*Summary of the values for* $pK_2$ *and* $K_2$*, calculated from measurements of five groups of solutions at temperatures from 0° to 60° C*

| *t* | Series A 1 to 6 | Series A 7 to 16 | Series B | Series B* | Series C | $pK_2$ (average) | $K_2 \times 10^8$ |
|---|---|---|---|---|---|---|---|
| °C | | | | | | | |
| 0 | 7.3133 | 7.3147 | 7.3145 | 7.3125 | 7.3139 | 7.314 ±.0012 | 4.85 |
| 5 | 7.2806 | 7.2818 | 7.2815 | 7.2817 | 7.2806 | 7.281 ±.0010 | 5.24 |
| 10 | 7.2538 | 7.2545 | 7.2540 | 7.2544 | 7.2533 | 7.254 ±.0010 | 5.57 |
| 15 | 7.2295 | 7.2303 | 7.2307 | 7.2308 | 7.2305 | 7.230 ±.0012 | 5.89 |
| 20 | 7.2114 | 7.2136 | 7.2127 | 7.2134 | 7.2129 | 7.213 ±.0010 | 6.12 |
| 25 | 7.1978 | 7.1983 | 7.1988 | 7.1977 | 7.1972 | 7.198 ±.0010 | 6.34 |
| 30 | 7.1880 | 7.1913 | 7.1888 | 7.1895 | 7.1909 | 7.190 ±.0013 | 6.46 |
| 35 | 7.1847 | 7.1862 | 7.1854 | 7.1853 | 7.1856 | 7.185 ±.0015 | 6.53 |
| 40 | 7.1798 | 7.1830 | 7.1811 | 7.1819 | 7.1822 | 7.182 ±.0015 | 6.58 |
| 45 | 7.1796 | 7.1818 | 7.1803 | 7.1816 | 7.1818 | 7.181 ±.0015 | 6.59 |
| 50 | 7.1817 | 7.1841 | 7.1835 | 7.1844 | 7.1851 | 7.184 ±.0017 | 6.55 |
| 55 | 7.1853 | 7.1873 | 7.1869 | 7.1888 | 7.1893 | 7.188 ±.0020 | 6.49 |
| 60 | 7.1940 | 7.1954 | 7.1943 | 7.1973 | 7.1981 | 7.196 ±.0022 | 6.37 |

The $pK_2$ values found in 10 different investigations by conductance and emf methods are compared in table 6. The temperature is 25° C in each case.

TABLE 6.—*Comparison of measurements of* $pK_2$ *at 25° C*

| Reference | Year | Method | $pK_2$ |
|---|---|---|---|
| Abbott and Bray [32] | 1909 | Conductance | [a] 6.69 |
| Michaelis and Garmendia [33] | 1914 | emf (with liquid junction) | [ab] 7.07 |
| Michaelis and Krüger [34] | 1921 | do | [ab] 7.11 |
| Prideaux and Ward [35] | 1924 | do | [ab] 7.17 |
| Cohn [36] | 1927 | do | [abc] 7.17 |
| Bjerrum and Unmack [4] | 1929 | do | 7.207 |
| Nims [5] | 1933 | emf (without liquid junction) | 7.206 |
| Guggenheim and Schindler [37] | 1934 | emf (with liquid junction) | 7.228 |
| Sima [38] | 1939 | do | 7.02 |
| This investigation | | emf (without liquid junction) | 7.198 |

[a] Value at 18° corrected to 25° by use of temperature coefficient of $pK_1$ from data of this investigation. $pK_{18}-pK_{25}=0.02$.
[b] Recalculated by Bjerrum and Unmack [4] by the use of 0.3360 v for the potential of the 0.1 *N* calome reference electrode.
[c] Calculated by Cohn from earlier results [33, 34, 39].

A large-scale graph of $pK_2$ with respect to $t$ (fig. 7) shows that the dissociation constant reaches a maximum value of $6.593 \times 10^{-8}$ ($pK_2$ reaches a minimum value of 7.1809) at a temperature of 43.75° C. Harned and Embree [40] have assumed that the plot of $pK$ with respect to $t$ is a parabola, an assumption that has been verified by experiment in the cases of several weak electrolytes, particularly

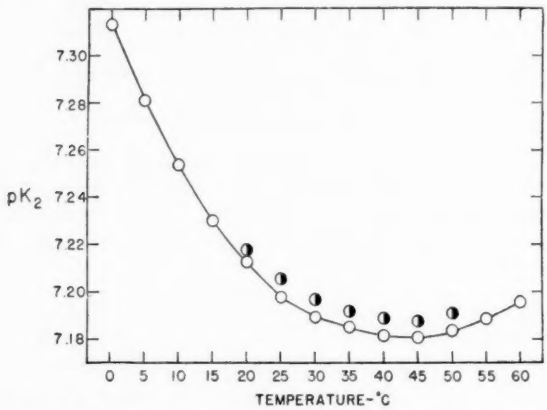


FIGURE 7.—*Plot of the second dissociation constant as a function of temperature.*
The values given by Nims [5] are included as half-shaded circles.

for temperatures close to that for the minimum, $\theta$. Their empirical equation for the variation of $pK$ with temperature in this range is

$$pK_t = pK_{min} + 5 \times 10^{-5}(t-\theta)^2. \quad (16)$$

Later, Owen [41] generalized eq 16 as follows:

$$pK_t = pK_{min} + p(t-\theta)^2. \quad (17)$$

The experimental $pK_2$ values are given by eq 16 with an average deviation of 0.008. When a value of $6.2 \times 10^{-5}$ is assigned to $p$, $pK_2$ is represented by eq 17 with a mean deviation of 0.003. In both cases the values from 20° to 60° C fit acceptably, but below 20° these equations leave much to be desired.

Recently, Harned and Robinson [42] suggested an equation for the variation of p$K$ with absolute temperature, $T$, which is based upon the observation that electromotive forces of the hydrogen–silver-chloride cell (and consequently $\Delta F$, the change of free energy in the cell)[12] are quadratic functions of temperature, within the error of the experiments. This assumption requires that $\Delta F°$, the free-energy change for the dissociation of 1 mole of $H_2PO_4^-$ in the standard state, shall also be a quadratic function of temperature and leads to an empirical equation for the variation of p$K_2$ with $T$:

$$pK_2=\frac{A}{T}+B+CT. \tag{18}$$

The average values of p$K_2$ given in table 5 were used to obtain the numerical values of the constants of eq 18 by the method of least squares. With a mean deviation of 0.0013 at the 13 temperatures, p$K_2$ is given by the equation

$$pK_2=\frac{1979.5}{T}-5.3541+0.019840T. \tag{19}$$

## VI. THERMODYNAMIC QUANTITIES

Thermodynamic quantities for the second dissociation equilibrium of phosphoric acid can be computed from the parameters $A$, $B$, and $C$ of the Harned and Robinson equation.

Values of the standard change of free energy, $\Delta F°$, for the process, $H_2PO_4^-=H^++HPO_4^=$; the standard change in heat content, $\Delta H°$; the standard entropy change, $\Delta S°$; and the change in heat capacity, $\Delta C_p°$, accompanying the dissociation of 1 mole of $H_2PO_4^-$ are given in table 7. These numerical values were computed from the equations

$$\Delta F°=-RT\ln K_2=2.3026R(A+BT+CT^2) \tag{20}$$
$$=9057-24.50T+0.09078T^2$$

$$\Delta S°=-(d\Delta F°/dT)=2.3026R(-B-2CT) \tag{21}$$
$$=24.5-0.1816T$$

$$\Delta H°=\Delta F°+T\Delta S°=2.3026R(A-CT^2) \tag{22}$$
$$=9057-0.09078T^2$$

$$\Delta C_p°=d\Delta H°/dT=2.3026R(-2CT)$$
$$=-0.1816T \tag{23}$$

TABLE 7.—*Thermodynamic quantities for the process:* $H_2PO_4^-=H^++HPO_4^=$

| $t$ | $\Delta F°$ | | $\Delta H°$ | | $\Delta S°$ | | $\Delta C_p°$ | |
|---|---|---|---|---|---|---|---|---|
| | *Int. j* | *cal* | *Int. j* | *cal* | *Int. j deg*$^{-1}$ | *cal deg*$^{-1}$ | *Int. j deg*$^{-1}$ | *cal deg*$^{-1}$ |
| 0 | 38,231 | 9,139 | 9,555 | 2,284 | −105.0 | −25.1 | −207.5 | −49.6 |
| 5 | 38,763 | 9,266 | 8,509 | 2,034 | −108.8 | −26.0 | −211.3 | −50.5 |
| 10 | 39,319 | 9,399 | 7,442 | 1,779 | −112.5 | −26.9 | −215.0 | −51.4 |
| 15 | 39,892 | 9,536 | 6,359 | 1,520 | −116.3 | −27.8 | −218.8 | −52.3 |
| 20 | 40,482 | 9,677 | 5,254 | 1,256 | −120.1 | −28.7 | −222.6 | −53.2 |
| 25 | 41,093 | 9,823 | 4,129 | 987 | −123.8 | −29.6 | −226.3 | −54.1 |
| 30 | 41,720 | 9,973 | 2,987 | 714 | −127.6 | −30.5 | −230.1 | −55.0 |
| 35 | 42,369 | 10,128 | 1,828 | 437 | −131.4 | −31.4 | −234.3 | −56.0 |
| 40 | 43,038 | 10,288 | 648 | 155 | −135.5 | −32.4 | −238.0 | −56.9 |
| 45 | 43,724 | 10,452 | −552 | −132 | −139.3 | −33.3 | −241.8 | −57.8 |
| 50 | 44,427 | 10,620 | −1,770 | −432 | −143.1 | −34.2 | −245.6 | −58.7 |
| 55 | 45,155 | 10,794 | −3,004 | −718 | −146.8 | −35.1 | −249.3 | −59.6 |
| 60 | 45,895 | 10,971 | −4,263 | −1,019 | −150.6 | −36.0 | −253.1 | −60.5 |

[12] For this cell, $(d\Delta F/dt)=-F(dE/dt)$.

A value of $R$ of 8.3127 Int. j $deg^{-1}$ $mole^{-1}$ [19] was used to obtain the thermodynamic quantities in International joules. For comparison with data in the literature, which are often listed in calories, values of the thermodynamic quantities are also given in terms of that unit, 1 calorie being taken as 4.1833 Int. j, as recommended by the International Union of Chemistry [43].

Figure 8 is a graph of $\Delta H°$, the heat of dissociation, as a function of temperature in the range 0° to 60° C.

The $pK_2$ values found by Nims [5] from measurements of the hydrogen–silver-chloride cell from 20° to 50° C have been fitted to an equation of the Harned-Robinson form and the thermodynamic quantities calculated for comparison with those of table 7. At 25° C, Nims found $pK_2=7.206$, a value higher by 0.008 than the value found in this investigation. At this temperature, −30.2 cal $deg^{-1}$ was found for $\Delta S°$; 817 cal for $\Delta H°$; and −45.2 cal $deg^{-1}$ for $\Delta C_p°$.

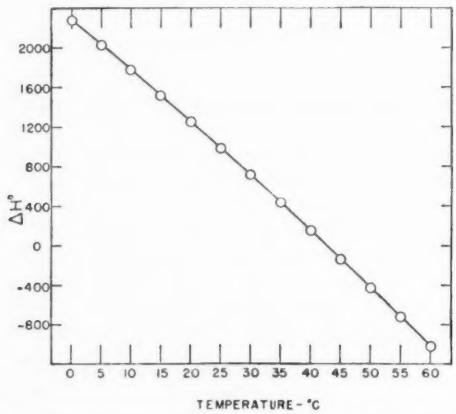


FIGURE 8.—*Heat of dissociation of dihydrogen phosphate ion, in calories, as a function of temperature.*

Figure 7, in which the $pK_2$ values of Nims are included as half-shaded circles, shows that the change of $pK_2$ with respect to temperature is substantially the same, between 20° and 50° C, for the two independent determinations. The values of Nims are 0.005 to 0.008 unit higher at each temperature than the present results.

Measurements of the dissociation constant should be made over as wide a range of temperatures as possible if the thermodynamic quantities derived from the temperature coefficient are to be obtained with the highest precision. It is furthermore particularly desirable that measurements be made at temperatures as far as possible from that of the minimum in $pK$, both above and below the temperature of the minimum.

The numerical values of table 7, for example, would have been quite different if they had been derived from measurements at only seven temperatures. For a comparison of $\Delta H°$, $\Delta S°$, and $\Delta C_p°$ calculated from the two independent determinations of $pK_2$ between 20° and 50° C, the $pK_2$ values found in this investigation for these temperatures were fitted to eq 18, and the derived thermodynamic quantities

were computed from $A$, $B$, and $C$, as before. Neglect of the measurements below 20° and above 50° C resulted in significant changes, and the values of the thermodynamic quantities were in each case closer to those derived from the measurements of Nims than are those of table 7. Thus $\Delta S°$ becomes $-30.0$ cal deg$^{-1}$ at 25° C, $\Delta H°$ is 878 cal, and $\Delta C_p°$ becomes $-48.4$ cal deg$^{-1}$ when the data at the lowest and highest temperatures are not used.

## VII. pH VALUES OF PHOSPHATE SOLUTIONS

Equation 14 was used to calculate the pH number for each of the solutions used in the cells. The values for series A are given in table 8, for series B and B* in table 9, and for series C solutions in table 10. It is noteworthy that each of these solutions is a suitable standard for pH.

TABLE 8.—pH *values of mixtures of sodium dihydrogen phosphate* ($m_1$), *disodium hydrogen phosphate* ($m_2$), *and sodium chloride* ($m_3$): *series A*

| Solution number | $m_1 = m_3$ | $m_2$ | pH | | | | |
|---|---|---|---|---|---|---|---|
| | | | 0° | 5° | 10° | 15° | 20° |
| A1 | 0.09079 | 0.08961 | 6.749 | 6.720 | 6.696 | 6.674 | 6.653 |
| A2 | .07340 | .07245 | 6.782 | 6.751 | 6.727 | 6.703 | 6.683 |
| A3 | .05507 | .05435 | 6.828 | 6.798 | 6.773 | 6.749 | 6.729 |
| A4 | .03726 | .03678 | 6.886 | 6.851 | 6.828 | 6.806 | 6.781 |
| A5 | .03017 | .02977 | 6.911 | 6.882 | 6.855 | 6.831 | 6.810 |
| A6 | .010491 | .010354 | 7.041 | 7.009 | 6.981 | 6.957 | 6.937 |
| A7 | .09079 | .08915 | 6.751 | 6.719 | 6.696 | 6.673 | 6.653 |
| A8 | .07475 | .07340 | 6.781 | 6.749 | 6.725 | 6.701 | 6.682 |
| A9 | .05199 | .05105 | 6.831 | 6.805 | 6.779 | 6.756 | 6.735 |
| A10 | .03592 | .03527 | 6.889 | 6.857 | 6.831 | 6.807 | 6.788 |
| A11 | .018456 | .018122 | 6.977 | 6.944 | 6.916 | 6.892 | 6.873 |
| A12 | .015090 | .014818 | 7.001 | 6.968 | 6.940 | 6.916 | 6.896 |
| A13 | .010151 | .009968 | 7.044 | 7.012 | 6.984 | 6.960 | 6.941 |
| A14 | .008598 | .008442 | 7.062 | 7.028 | 7.000 | 6.976 | 6.958 |
| A15 | .005978 | .005870 | 7.097 | 7.062 | 7.034 | 7.010 | 6.991 |
| A16 | .004213 | .004137 | 7.125 | 7.092 | 7.063 | 7.038 | 7.020 |

| Solution number | pH | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 25° | 30° | 35° | 40° | 45° | 50° | 55° | 60° |
| A1 | 6.634 | 6.620 | 6.613 | 6.603 | 6.614 | 6.610 | 6.608 | 6.612 |
| A2 | 6.666 | 6.651 | 6.644 | 6.633 | 6.640 | 6.639 | 6.637 | 6.641 |
| A3 | 6.711 | 6.698 | 6.690 | 6.680 | 6.686 | 6.683 | 6.682 | 6.686 |
| A4 | 6.766 | 6.751 | 6.743 | 6.735 | 6.738 | 6.735 | 6.734 | 6.738 |
| A5 | 6.793 | 6.781 | 6.774 | 6.766 | 6.769 | 6.768 | 6.769 | 6.774 |
| A6 | 6.921 | 6.909 | 6.902 | 6.808 | 6.895 | 6.894 | 6.807 | 6.900 |
| A7 | 6.633 | 6.621 | 6.613 | 6.603 | 6.612 | 6.610 | 6.608 | 6.611 |
| A8 | 6.662 | 6.650 | 6.638 | 6.631 | 6.639 | 6.635 | 6.633 | 6.637 |
| A9 | 6.717 | 6.709 | 6.700 | 6.692 | 6.696 | 6.693 | 6.693 | 6.697 |
| A10 | 6.769 | 6.759 | 6.751 | 6.744 | 6.745 | 6.744 | 6.742 | 6.745 |
| A11 | 6.854 | 6.846 | 6.838 | 6.832 | 6.832 | 6.832 | 6.831 | 6.836 |
| A12 | 6.879 | 6.868 | 6.859 | 6.853 | 6.853 | 6.852 | 6.852 | 6.856 |
| A13 | 6.923 | 6.912 | 6.904 | 6.898 | 6.898 | 6.898 | 6.899 | 6.906 |
| A14 | 6.940 | 6.931 | 6.924 | 6.918 | 6.917 | 6.917 | 6.918 | 6.923 |
| A15 | 6.974 | 6.966 | 6.958 | 6.953 | 6.952 | 6.953 | 6.953 | 6.959 |
| A16 | 7.003 | 6.995 | 6.987 | 6.982 | 6.981 | 6.982 | 6.982 | 6.987 |

TABLE 9.—pH *values of mixtures of sodium dihydrogen phosphate* ($m_1$), *disodium hydrogen phosphate* ($m_2$), *and sodium chloride* ($m_3$): *series B; and the* pH *values of mixtures of potassium dihydrogen phosphate* ($m_1$), *disodium hydrogen phosphate* ($m_2$), *and sodium chloride* ($m_3$); *series B**

SERIES B

| Solution number | $m_1 = m_3$ | $m_2$ | pH | | | | |
|---|---|---|---|---|---|---|---|
| | | | 0° | 5° | 10° | 15° | 20° |
| B1 | 0.09079 | 0.05789 | 6.599 | 6.566 | 6.540 | 6.516 | 6.497 |
| B2 | .07410 | .04725 | 6.634 | 6.603 | 6.578 | 6.557 | 6.535 |
| B3 | .05294 | .03375 | 6.678 | 6.647 | 6.622 | 6.599 | 6.578 |
| B4 | .03459 | .02205 | 6.737 | 6.704 | 6.678 | 6.654 | 6.634 |
| B5 | .02343 | .014937 | 6.785 | 6.755 | 6.728 | 6.705 | 6.684 |
| B6 | .014911 | .009507 | 6.839 | 6.805 | 6.778 | 6.754 | 6.733 |
| B7 | .009764 | .006226 | 6.886 | 6.853 | 6.825 | 6.802 | 6.783 |
| B8 | .007546 | .004811 | 6.908 | 6.873 | 6.844 | 6.820 | 6.800 |
| B9 | .005365 | .003420 | 6.939 | 6.905 | 6.876 | 6.853 | 6.833 |

SERIES B*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| B*1 | 0.09077 | 0.05787 | 6.597 | 6.568 | 6.543 | 6.521 | 6.501 |
| B*2 | .05151 | .03284 | 6.682 | 6.652 | 6.625 | 6.602 | 6.582 |
| B*3 | .04604 | .02935 | 6.697 | 6.668 | 6.642 | 6.618 | 6.597 |
| B*4 | .02877 | .018341 | 6.766 | 6.730 | 6.703 | 6.678 | 6.658 |
| B*5 | .009373 | .005976 | 6.886 | 6.855 | 6.827 | 6.803 | 6.784 |
| B*6 | .006059 | .003863 | 6.922 | 6.891 | 6.864 | 6.840 | 6.821 |
| B*7 | .004099 | .002614 | 6.955 | 6.924 | 6.896 | 6.873 | 6.854 |
| B*8 | .002835 | .0018073 | 6.980 | 6.949 | 6.921 | 6.897 | 6.877 |

SERIES B—Continued

| Solution number | pH | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 25° | 30° | 35° | 40° | 45° | 50° | 55° | 60° |
| B1 | 6.481 | 6.470 | 6.462 | 6.454 | 6.462 | 6.459 | 6.456 | 6.460 |
| B2 | 6.515 | 6.502 | 6.495 | 6.479 | 6.487 | 6.487 | 6.487 | 6.490 |
| B3 | 6.559 | 6.545 | 6.538 | 6.531 | 6.534 | 6.533 | 6.530 | 6.532 |
| B4 | 6.617 | 6.603 | 6.596 | 6.589 | 6.590 | 6.589 | 6.588 | 6.592 |
| B5 | 6.667 | 6.655 | 6.651 | 6.645 | 6.644 | 6.646 | 6.646 | 6.650 |
| B6 | 6.717 | 6.704 | 6.694 | 6.696 | 6.688 | 6.689 | 6.689 | 6.693 |
| B7 | 6.766 | | | | | | | |
| B8 | 6.785 | | | | | | | |
| B9 | 6.818 | 6.805 | 6.799 | 6.795 | 6.794 | 6.794 | 6.798 | 6.801 |

SERIES B*—Continued

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| B*1 | 6.482 | 6.470 | 6.460 | 6.452 | 6.459 | 6.456 | 6.455 | 6.460 |
| B*2 | 6.564 | 6.551 | 6.543 | 6.537 | 6.541 | 6.539 | 6.539 | 6.544 |
| B*3 | 6.579 | 6.567 | 6.558 | 6.548 | 6.554 | 6.553 | 6.552 | 6.556 |
| B*4 | 6.640 | 6.630 | 6.622 | 6.615 | 6.617 | 6.615 | 6.616 | 6.620 |
| B*5 | 6.766 | 6.755 | 6.750 | 6.744 | 6.744 | 6.745 | 6.747 | 6.753 |
| B*6 | 6.803 | 6.794 | 6.789 | 6.785 | 6.785 | 6.787 | 6.790 | 6.797 |
| B*7 | 6.835 | 6.827 | | | | | | |
| B*8 | 6.860 | 6.850 | 6.845 | 6.839 | 6.837 | 6.839 | 6.842 | 6.848 |

TABLE 10.—pH *values of mixtures of sodium dihydrogen phosphate* ($m_1$), *disodium hydrogen phosphate* ($m_2$), *and sodium chloride* ($m_3$): *series C*

| Solution number | $m_1=m_2$ | $m_3$ | pH | | | | |
|---|---|---|---|---|---|---|---|
| | | | 0° | 5° | 10° | 15° | 20° |
| C1 | 0.09079 | 0.13882 | 6.895 | 6.864 | 6.841 | 6.821 | 6.800 |
| C2 | .06661 | .10185 | 6.945 | 6.915 | 6.890 | 6.869 | 6.848 |
| C3 | .04820 | .07371 | 6.996 | 6.965 | 6.940 | 6.918 | 6.897 |
| C4 | .02578 | .03943 | 7.088 | 7.056 | 7.029 | 7.006 | 6.986 |
| C5 | .011957 | .018283 | 7.185 | 7.153 | 7.125 | 7.102 | 7.082 |
| C6 | .007914 | .012102 | 7.232 | 7.199 | 7.171 | 7.147 | 7.127 |
| C7 | .004944 | .007560 | ---- | 7.242 | 7.215 | 7.193 | 7.173 |
| C8 | .002943 | .004501 | 7.323 | 7.290 | 7.261 | 7.239 | 7.218 |
| C9 | .0019314 | .002953 | 7.350 | 7.318 | 7.290 | 7.267 | 7.248 |

| Solution number | pH | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 25° | 30° | 35° | 40° | 45° | 50° | 55° | 60° |
| C1 | 6.779 | 6.767 | 6.757 | 6.751 | 6.760 | 6.758 | 6.756 | 6.759 |
| C2 | 6.830 | 6.817 | 6.809 | 6.799 | 6.808 | 6.807 | 6.805 | 6.809 |
| C3 | 6.878 | 6.866 | 6.855 | 6.846 | 6.853 | 6.851 | 6.850 | 6.856 |
| C4 | 6.966 | 6.957 | 6.947 | 6.939 | 6.944 | 6.944 | 6.944 | 6.949 |
| C5 | 7.064 | 7.054 | 7.046 | 7.040 | 7.040 | 7.040 | 7.043 | 7.050 |
| C6 | 7.110 | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| C7 | 7.154 | 7.148 | 7.142 | ---- | ---- | ---- | ---- | ---- |
| C8 | 7.202 | 7.195 | 7.186 | 7.182 | 7.181 | 7.181 | 7.185 | 7.190 |
| C9 | 7.229 | 7.224 | 7.217 | 7.213 | 7.212 | 7.214 | 7.216 | 7.220 |

The change of pH of 18 representative solutions with change in temperature is shown graphically in figures 9, 10, and 11.

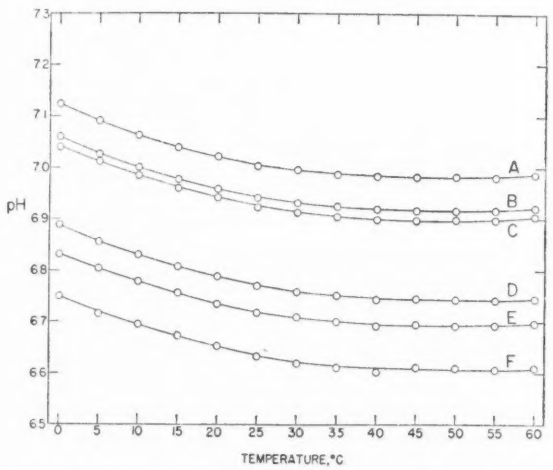


FIGURE 9.—pH *values of series A solutions as a function of temperature.*
Curves *A* to *F* represent pH values of solutions A16, A14, A13, A10, A9, and A7, respectively.

Writing the mass-action constant for the second dissociation (eq 8a) in the logarithmic form and combining it with eq 11, we have

$$\mathrm{pH}=\mathrm{p}K_2-\log(m_{\mathrm{H_2PO_4}}/m_{\mathrm{HPO_4}})-3A\sqrt{\mu}/(1+Ba_i\sqrt{\mu}). \qquad (24)$$

With the use of eq 24, p$K_2$ from table 5, and the values of $3A$ and $Ba_i$ from table 4, it is possible to compute pH values at 0° to 60° C

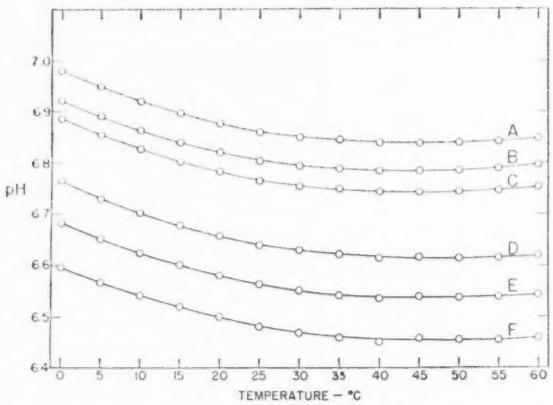


FIGURE 10.—pH *values of series B* solutions as a function of temperature.*
Curves *A* to *F* represent pH values of solutions B*8, B*6, B*5, B*4, B*2, and B*1, respectively.

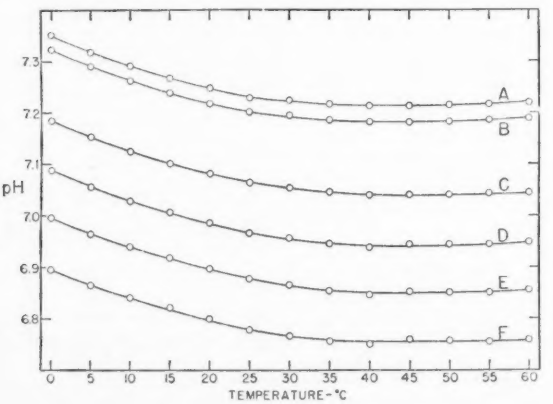


FIGURE 11.—pH *values of series C solutions as a function of temperature.*
Curves *A* to *F* represent solutions C9, C8, C5, C4, C3, and C1, respectively.

for phosphate-chloride mixtures in which $m_{\mathrm{Cl}}=m_{\mathrm{H_2PO_4}}$. Values of the pH computed from eq 24 for series A solutions 11 to 20 are in accord to 0.001 unit with those derived from eq 14.

When the ionic strength is less than 0.5 and the ratio of the molality of primary phosphate ion to that of secondary phosphate ion lies between 0.5 and 2, an error of less than $\pm 0.003$ unit may be ascribed to the pH values calculated from eq 24, as also to those listed in tables 8, 9, and 10.

It is evident (table 4) that substitution of potassium dihydrogen phosphate (series B*) for the corresponding sodium salt (series B) affects only the $\beta$ value. The fact that a $\beta\mu$ term does not appear in eq 24 suggests that solutions which differ only by the substitution of the potassium salt for the sodium salt should have identical pH values, provided the same $a_t$ value applies to both types of mixtures.[13] This conclusion is supported by the agreement between the pH values for solutions B1 and B*1, which show a mean difference of only 0.002 unit for the 13 temperatures (see table 9).

A mixture of 0.02 *m* potassium dihydrogen phosphate, 0.03 *m* disodium hydrogen phosphate, and 0.02 *m* sodium chloride has a pH value very nearly 7 at room temperature. This solution may be used at temperatures between 20° and 30° C for the calibration of glass electrodes at a pH of 7, with an accuracy of $\pm 0.02$ unit. If a tolerance of $\pm 0.032$ unit is allowable, it may be used at all temperatures between 15° and 60° C. Table 11 gives pH values of this solution at 13 temperatures between 0° and 60° C. The buffer is prepared by dissolving 2.722 g of potassium dihydrogen phosphate, 4.260 g of anhydrous disodium hydrogen phosphate, and 1.169 g of sodium chloride in 1,000 g of freshly boiled distilled water (1002 . 94 ml at 25° C).

The change of pH at 25° C with molality of disodium hydrogen phosphate for four solutions in which the molalities of sodium dihydrogen phosphate and sodium chloride are both 0.03 is shown in table 12.

TABLE 11.—pH *values of the mixture* $KH_2PO_4$ *(0.02 m),* $Na_2HPO_4$ *(0.03 m),* NaCl *(0.02 m) from 0° to 60° C*

| *t* | pH | *t* | pH |
|---|---|---|---|
| ° *C* | | ° *C* | |
| 0 | 7.115 | 35 | 6.975 |
| 5 | 7.083 | 40 | 6.968 |
| 10 | 7.056 | 45 | 6.970 |
| 15 | 7.032 | 50 | 6.970 |
| 20 | 7.012 | 55 | 6.970 |
| 25 | 6.994 | 60 | 6.974 |
| 30 | 6.983 | | |

TABLE 12.—pH *values at 25° C for phosphate-chloride mixtures having the same molalities of* $NaH_2PO_4$ *and* NaCl ($m_1 = m_3$) *but different molalities of* $Na_2HPO_4$ ($m_2$)

| $m_1 = m_3$ | $m_2$ | pH |
|---|---|---|
| 0.03 | 0.02 | 6.652 |
| .03 | .03 | 6.799 |
| .03 | .04 | 6.899 |
| .03 | .05 | 6.975 |

In order that a precision of $\pm 0.003$ unit in the pH value may be attained, the buffer solutions should be carefully prepared from tested samples of phosphates, pure sodium chloride, and carbon-dioxide-free water. Potassium dihydrogen phosphate, sodium dihydrogen phosphate, and disodium hydrogen phosphate should be recrystallized from freshly boiled distilled water, or preferably water of conductivity

[13] For the mixtures composed entirely of sodium salts, the $\beta$ value appears to be a linear function of the buffer ratio. A further investigation of specific salt effects on $a_t$ and $\beta$ values will be of importance.

grade. Careful ignition of samples of potassium dihydrogen phosphate to constant weight should give a loss in weight of 13.22 to 13.30 percent. The loss in weight on ignition of sodium dihydrogen phosphate and disodium hydrogen phosphate should be 15.00 to 15.08 percent and 6.34 to 6.42 percent, respectively. It is desirable that the absence of carbonate from the secondary phosphate be affirmed by analysis. Disodium hydrogen phosphate should be kept in a desiccator or dried at 110° to 120° C before use.

Precipitation of sodium chloride from its saturated aqueous solution with dry hydrogen chloride has been found to be a more satisfactory means of purification than recrystallization from water. The salt must then be fused in platinum to remove occluded acid. Traces of bromide must be absent from all buffer solutions in which the silver-chloride electrode is to be employed.

For routine work, buffer solutions whose pH values were correct to $\pm 0.01$ unit have been prepared from reagent-grade chemicals and freshly boiled distilled water. Electromotive-force measurements of hydrogen–silver-chloride cells containing 16 phosphate-chloride mixtures prepared in this way were made at 25° C. The "experimental" pH values, computed from the emf by eq 14 with the use of the ionic parameters given in table 4, agreed on the average to 0.005 unit with those calculated by eq 24. The pH values of these solutions ranged from 7.2 to 7.8.

It should be emphasized, however, that a practical pH assembly with liquid junction, properly calibrated with a buffer of accurate pH value, cannot be relied upon to yield the correct values for the pH of unknown solutions that may have compositions, activities, and ion mobilities quite different from those of the standard [1].

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WASHINGTON, October 29, 1942.

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RESEARCH PAPER RP1525

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# MINIATURE GEIGER-MÜLLER COUNTER

By Leon F. Curtiss

ABSTRACT

A miniature Geiger-Müller tube counter having a tube 0.8 mm in internal diameter is described. This "hypodermic-needle" type of counter has been found useful in locating and measuring a well-defined beam of gamma radiation. It could also be used to measure a beam of hard X-rays reflected from a crystal. Another suggested use is direct insertion into specimens, such as living biological material.

There are many applications for which a Geiger-Müller counter of very small size would be useful. Where it is desirable to measure and locate a narrow beam of radiation, it would be very convenient to have a counter approximately the size of the cross section of the beam. This requires a counter of the order of 1 mm in diameter. The author knows of no previous attempts to construct counters of such size.

The ease with which thoroughly reliable counters containing alcohol vapor and argon may be constructed led to the trial of small counters. No difficulty was encountered in constructing counters with an internal diameter of 3 mm. Counters of this size give slightly larger pulses than is obtained from counters 2 or 3 cm in diameter. They also show a reasonable plateau and are quite stable. Counters of this diameter would not serve to locate a well-defined beam of radiation with sufficient precision for some purposes.

Encouraged by the results with the 3-mm counters, the author constructed the counter shown in figure 2. The No. 2 sewing needle is included in the picture for size comparison. The tube of the counter has an internal diameter of 0.8 mm and a length of about 3 mm. The central wire is tungsten, 0.05 mm in diameter. The filling gas is a mixture of amyl acetate vapor and argon at about 4-cm pressure.

This counter has an extremely low blank, averaging around 20 pulses per hour. The pulses are even larger than those from the 3-mm counters. This increase of pulse size with decrease of tube diameter could be expected from the known fact that the ionization is confined to a thin sheath near the central wire. The thickness of this sheath is increased as the tube becomes smaller, since the ratio of maximum to minimum gradient is smaller for the counter tube of smaller diameter.

The plateau for this counter is shown in figure 1. Although it is considerably steeper than for larger counters, this counter yields good results when operated from a stabilized voltage. This particular

counter has been in use for several months with no sign of deterioration.

The shape of the counter resembles a large hypodermic needle, which suggests another type of use. It could be introduced directly into material to be tested and therefore increase the sensitivity of the measurement. This could be of value in studying biological specimens. It could even be used with live animals. No attempts have been made to construct counters of smaller diameter, but it seems likely they could be made. The chief difficulty is in devising a method of locating the central wire so that it does not touch the counter tube. Exact centering of this wire is not necessary, since the only precaution taken with the present counter was to make certain that the wire was not in contact with the tube.

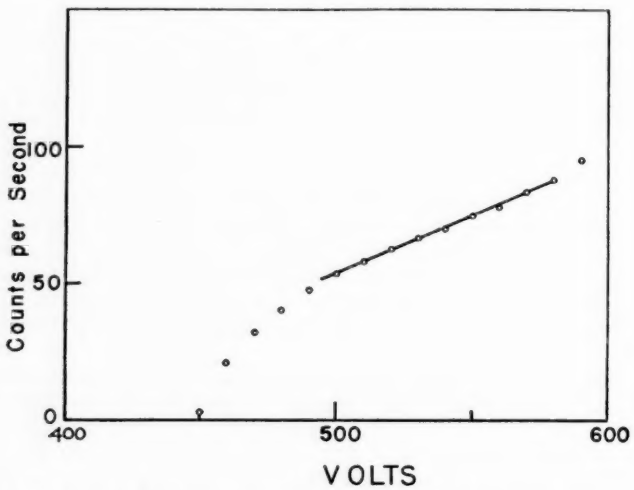


FIGURE 1.—*Hypodermic-needle-type Geiger-Müller counter.*

Further work is in progress in an effort to improve the characteristics of these miniature tube counters and to determine the lowest limit of tube diameter that can be used.

WASHINGTON, December 2, 1942.

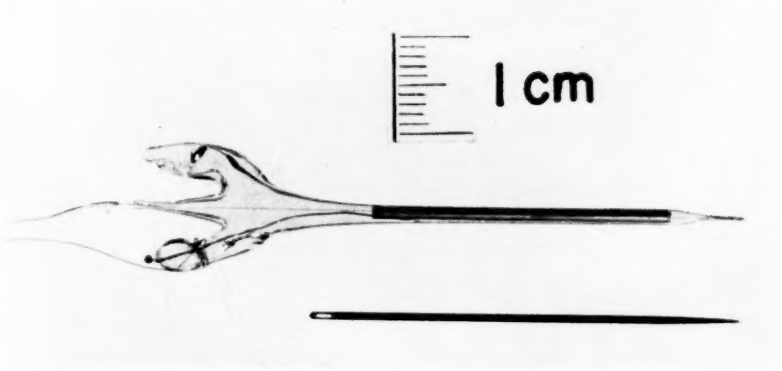


FIGURE 2. —*Miniature Geiger-Müller counter.*
The sewing needle is included for size comparison.

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